the half-life of 9×10^{-4} sec. as compared with $1-2 \times 10^{-3}$ sec. obtained for the hydrocarbon radicals[9] CH_3 and CH_2.

We made a few attempts to produce the NH radical from other sources. Cyanic acid appears to exist in the form[10] HNCO and might be expected therefore to produce the blue material when decomposed. However, cyanic acid was not decomposed in our apparatus even when the furnace temperature was raised to 1250°.

We also attempted to burn off two of the hydrogen atoms of ammonia with oxygen. Two experiments were performed, the first with ammonia containing 5 molar per cent. of oxygen and the second with oxygen containing 5 molar per cent. of ammonia but neither yielded any blue material.

At the present time we do not have much evidence as to the constitution of the blue substance. The first possibility is that it is the imine radical in the solid state in which each individual NH radical is loosely coupled with its neighbors. In favor of this is the observation that NH has a forbidden transition at 8502 cm.$^{-1}$. If we make the reasonable assumptions that restrictions are relaxed for the solid state and that there is widening of the band we would have absorption in the red and a blue solid.

A second possibility is that the blue solid is the much sought for diimide, HN=NH, the parent of all the organic azo compounds. Although Thiele[11] concluded that diimide does not exist, it has been frequently postulated[12] as an intermediate in various reactions such as for example the oxidation of hydrazine which under some conditions gives good yields of ammonium azide. The rather reasonable mechanism postulated is

$$H_2N{-}NH_2 \xrightarrow{O} HN{=}NH \longrightarrow {}^1/_2NH_4(N)_3$$

The fact that the blue compound is paramagnetic is consistent with the possibility of its being diimide which may be expected to have an electronic structure similar to oxygen.[13]

There is a further possibility that the blue compound consists of a mixture of the monomer and dimer or that it consists of still higher polymers[14] of NH but it seems that the best way at present to obtain unequivocal evidence of its constitution is to take X-ray photographs below −125°.

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[9] F. O. Rice and A. L. Glazebrook, THIS JOURNAL, **56**, 2381 (1934); F. O. Rice, W. R. Johnston and B. L. Evering, *ibid.*, **54**, 3535 (1932).

[10] J. Goubeau, *Ber.*, **68**, 912 (1935); S. Woo and T. Liu, *J. Chem. Phys.*, **3**, 544 (1935).

[11] J. Thiele, *Ann.*, **271**, 133 (1892).

[12] See R. E. Kirk and A. W. Browne, THIS JOURNAL, **50**, 341 (1928).

[13] See L. Pauling, *ibid.*, **53**, 3233 (1931).

[14] O. Dimroth and K. Pfister, *Ber.*, **43**, 2757 (1910), tried unsuccessfuly to prepare N_3H_3.

WASHINGTON, D. C.

RECEIVED MAY 5, 1951

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Ionization Equilibria of Derivatives of Triphenylchloromethane in Liquid Sulfur Dioxide

BY NORMAN N. LICHTIN AND PAUL D. BARTLETT

The equivalent conductances of triphenylchloromethane, its mono-*m*-methyl, mono-*p*-methyl, mono-*m*-*t*-butyl, mono-*p*-*t* butyl, di-*p*-*t*-butyl and tri-*p*-*t*-butyl derivatives and of 9-phenyl-9-chloro-10,10-dimethyl-9,10-dihydroanthracene have been measured in liquid sulfur dioxide at 0° over a wide range of concentrations. Similar data have been collected at −17° for triphenylchloromethane and its tri-*p*-*t*-butyl derivative. Values of $K_{\text{dissn.}}$ and Λ_0 have been calculated for all these compounds using Shedlovsky's method. $\Delta F^\circ_{0°}$ of dissociation has been calculated for all compounds of the series and $\Delta H^\circ_{0°}$ and $\Delta S^\circ_{0°}$ for those for which data at two temperatures are available. It has been demonstrated that for the five weakest electrolytes in the series, ion pair equilibria can be treated so as to make possible the interpretation of the measured dissociation constants in terms of electronic effects within the molecules and ions.

Introduction

It has been known for some time that triarylcarbonium ions (*e.g.*, triphenylcarbonium ion) are relatively stable and can be produced reversibly.[1] Investigations of the conductance of solutions in liquid sulfur dioxide of triarylmethyl halides, perchlorates, etc., have provided major evidence establishing this fact.[2–6] Ziegler and Wollschitt[4] measured the conductance of solutions in liquid sulfur dioxide of many such compounds over a wide concentration range (10^{-2} to 10^{-5} molar). They found that the introduction of one, two, or three *p*-methyl or *p*-methoxyl substituents into triphenylmethyl perchlorate caused only slight changes in the equivalent conductance curves and they deduced that these compounds are all strong electrolytes which differ in conductance only because of the different mobilities of the organic cations. This is supported by the work of Dilthey and Alfusz[7] who found that the mono-, di- and tri-*p*-methoxy derivatives of triphenylmethyl perchlorate form orange crystals and are therefore presumably ionic in the solid state. Ziegler and Wollschitt found that the electrolyte behavior of triarylmethyl chlorides is, in contrast, sharply dependent on the structures of the molecules. They concluded that their chlorides are not strong electrolytes but that an equilibrium exists in solution between molecules in which chlorine is covalently bound, ion pairs, and ions

$$Ar_3CCl_{(SO_2)} \rightleftarrows Ar_3C^+Cl^-_{(SO_2)} \rightleftarrows Ar_3C^+_{(SO_2)} + Cl^-_{(SO_2)}$$

Although they were unable to express their results

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 53–55.

[2] P. Walden, *Ber.*, **35**, 2018 (1902).

[3] M. Gomberg, *ibid.*, **35**, 2403 (1902).

[4] K. Ziegler and H. Wollschitt, *Ann.*, **479**, 90 (1930).

[5] K. Ziegler and W. Mathes, *ibid.*, **479**, 111 (1930).

[6] S. T. Bowden and T. L. Thomas, *J. Chem. Soc.*, 1242 (1940).

[7] W. Dilthey and W. Alfusz, *Ber.*, **62**, 2078 (1929).

in terms of equilibrium constants, direct comparison of conductance curves shows the relative effectiveness of various groups in promoting ionization of derivatives of triphenylchloromethane. Thus, *p*-phenyl, *p*-methyl and *p*-methoxyl have, respectively, increasing effects in enhancing ionization whereas nitro[5] reduces it. Two substituents are more effective than one; three are even more so.

The research reported here was undertaken in order to obtain new information bearing on the electronic influences of alkyl groups through a study of the conductivity in liquid sulfur dioxide of meta- and para-alkyl derivatives of triphenylchloromethane. The compounds investigated include triphenylchloromethane, its mono-, di- and tri-*p*-*t*-butyl, mono-*m*-*t*-butyl, mono-*p*-methyl and mono-*m*-methyl derivatives, as well as 9-phenyl-9-chloro-10,10-dimethyl-9,10-dihydroanthracene.

The measurements were carried out using a refined version of the method originated by Ziegler and Wollschitt.[4] All compounds were measured at 0°, two at −17° as well. Thermodynamic equilibrium constants have been calculated for all the compounds by means of Shedlovsky's method.[8,9] The significance of these constants relative to properties of the molecules and ions has been evaluated.

Experimental

The apparatus and general procedure were based upon the work of Ziegler and Wollschitt.[4]

The cell (Fig. 1) was similar to Ziegler's but was modified by inclusion of the solid introduction tube (A), the spray trap (J), and the long mercury-filled electrode wells (C, D). The cell was constructed of Pyrex glass. The electrode bulb volume (F and I) was about 30 cc. while that of the distillation bulb (K) was about 100 cc. The stiff platinum electrodes (G and H) were spot welded to tungsten wires which were sealed into the electrode wells (C and D). The electrodes were also embedded in a glass support. The graduated portion of the electrode arm (I) was a piece of a Pyrex buret which had been calibrated with water. The spray trap (J) consisted of a 7-cm. column of Pyrex helices ($^1/_8$" diameter). The electrodes were platinized in the usual manner.[10]

Ohio Chemical Co. sulfur dioxide was employed. The gas was dried by passing it either over phosphorus pentoxide (36") or over calcium chloride (24") and then Drierite (24"). It was then passed through a bubble counter containing either silicone fluid (Dow Corning No. 500) or mercury (triple distilled grade) and two dust and spray traps (held at room temperature) before passing into the cell.

For work at 0° a slush of shaved ice and water was used as a thermostat. Measurements at −17° were carried out in a thermostat which employed a stirred ice–sodium chloride slurry as cooling mixture. A stirred toluene-bath was immersed in the slurry. The temperature of the inner bath was maintained constant with the aid of a small heater connected to a toluene bulb thermoregulator through an electronic relay. This device controlled the temperature to ±0.1° but the average temperature of individual runs varied between −16.5 and −17°.

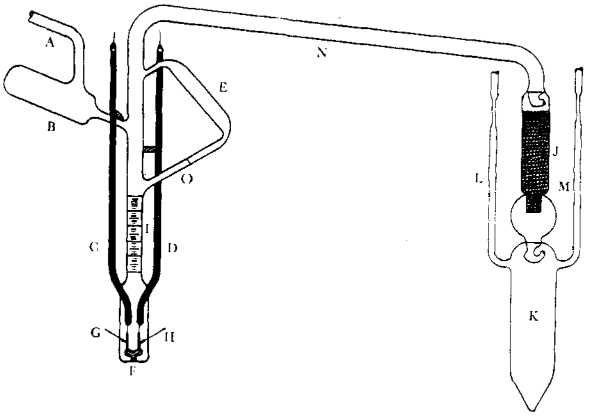

Fig. 1.—Conductivity cell.

The great majority of the measurements were made at 2000 cycles using a Jones bridge built by Leeds and Northrup.[11,12] Bridge balance was detected with an oscilloscope following the procedure and with the aid of the auxiliary apparatus described by Jones, Mysels and Juda.[13] A few of the runs were made using an Industrial Instruments Model RC-1 B Bridge. This instrument includes a 1000-cycle oscillator and an "electric eye" detector. It was used in conjunction with a variable air condenser.

Samples of solute, ranging from 10 to 400 mg. in size, were weighed to 0.01 mg. in weighing bottles that were so constructed that they could be inserted at least 2 cm. into tube A. Thus crystals were introduced directly into the cell with no possibility of transfer loss.

Throughout the work great care was observed to maintain the cell free of adsorbed electrolytes. At the beginning of the measurements and about every tenth or fifteenth run the entire cell was cleaned with chromic acid solution, rinsed with water, and adsorbed acids removed by filling it with 10% ammonium hydroxide and allowing it to stand for several hours. The cell was then rinsed exhaustively with distilled water followed by several rinsings with C.P. acetone and C.P. 30–60° petroleum ether. For all other runs only the organic solvents were employed. The well rinsed cell was then evacuated repeatedly to 0.1 mm. (through arm L), air, dried by passage through calcium chloride and then Drierite, being admitted each time. All of the cell except the electrode arm was heated with a bunsen flame during the pumping. A sample of solute was then introduced into the cell, arm A sealed off, and the whole system pumped at 0.1 mm. overnight. The vacuum arm (L) was then sealed off and sulfur dioxide admitted to the evacuated cell through arm M and condensed in the electrode bulb with the aid of an ice–sodium chloride bath. Arm M was then sealed off.

The solution was next poured back and forth into bulb B to assure homogeneity. After the electrode arm had been brought to constant temperature in a thermostat, as shown by the absence of resistance drifts (15 to 20 minutes), and a measurement performed, the solution was diluted in the cell. First, the entire cell was immersed in an ice-bath for about five minutes to minimize distillation during the next manipulation. Next, by suitable rotation of the cell, a fixed volume of solution was trapped in bulb E, the rest being discarded into the distillation bulb (K). The electrode arm was then immersed in an ice–sodium chloride-bath and bulb K warmed with a micro burner. Distillation (even boiling) was continued until about 1 cc. of solution remained. The cell was then rotated so that this flowed into arm L where it evaporated rapidly. Thus the distillation of solvent from very concentrated solutions into very dilute ones was prevented. After mixing the electrode arm contents thoroughly the cell was replaced in the thermostat. When runs were made at two temperatures, the −17° reading was made first. The solution volume was read on D for each point.

After six to eight dilutions had been carried out, the entire very dilute solution was poured over into bulb K and pure (colorless) solvent distilled back. The conductivity of the solvent was determined independently for each run. In

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

[9] Application of Shedlovsky's method to Ziegler and Wollschitt's data for tris-*p*-methoxyphenylmethyl perchlorate does not yield the desired straight line plot. Apparently the accuracy of their work is not sufficient for these calculations. Two of Ziegler's compounds (trityl chloride and its mono-*p*-methyl derivative) were remeasured in the present work. Discrepancies which increased as concentration decreased were observed.

[10] L. Michaelis in A. Weissberger, "Physical Methods of Organic Chemistry," 2d ed., Vol. I, Interscience Publishers, Inc., New York, N. Y., 1949, Pt. 2, p. 1722.

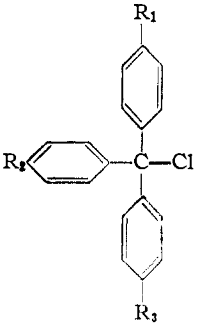
[11] G. Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928).

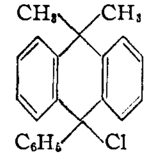
[12] P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

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

TABLE I

COMPOUNDS EMPLOYED



Sample	Substituents R_1	R_2	R_3	No. of runs	Melting range,[a] °C.	Melting range lit., °C.	Hydrolyzable chloride, % Found	Theory
1	H	H	H	4	111–112	112–113[i]	12.9	12.7
2[b,f]	H	H	H	1	....	112–113[i]	..	12.7
3[c]	H	H	H	1	110.2–112.4	112–113[i]	12.4	12.7
4[b,g]	H	H	D	1	....	......	..	12.7
5[c]	H	H	*m*-CH_3	2	71.5–72.5	71[j]	12.0	12.1
6[c]	H	H	*m*-*t*-Bu	2	73.5–75[f]	......	10.7	10.6
7[d]	H	H	*p*-CH_3	2	98.0–99.0	99[k]	..	12.1
8[d]	H	H	*p*-CH_3	2	98.8–99.2	99[k]	11.8	12.1
9[e]	H	H	*p*-*t*-Bu	2	134.9–135.8	133–134[l]	10.6	10.6
10[c]	H	H	*p*-*t*-Bu	3	135.5–136.7	133–134[l]	10.3	10.6
11[e]	H	*p*-*t*-Bu	*p*-*t*-Bu	3	164.1–164.6	162–163[m]	9.2	9.1
12[d]	H	*p*-*t*-Bu	*p*-*t*-Bu	1	164.1–164.6	162–163[m]	9.1	9.1
13[e]	*p*-*t*-Bu	*p*-*t*-Bu	*p*-*t*-Bu	4	dec.[h]	259–260[m]	8.0	7.9
14[d]	*p*-*t*-Bu	*p*-*t*-Bu	*p*-*t*-Bu	3	dec.[h]	259–260[m]	7.9	7.9
15[a]				2	163.5–164.5	......	11.0	11.1

[a] Anschütz thermometers. [b] Chlorides supplied by Dr. William F. Sager. [c] Supplied by Dr. George B. De La Mater. Sample 5 was supplied as carbinol, all others as chlorides. [d] Supplied by Professor C. S. Marvel. Sample 14 was supplied as carbinol, all others as chlorides. [e] Chlorides supplied by Mrs. M. C. Roha. [f] Prepared in the same manner employed in making mono-*p*-deuterotriphenylchloromethane. [g] Analyzed by Dr. W. F. Sager for deuterium and found to contain 93% of the theoretical amount. [h] The observed melting point of this compound depends on the temperature of the m.p. block when the sample is introduced. Thus with block temperature increasing 1° per minute, introduction at 263° gives m.p. 267.8–271.0°; 268° gives m.p. 270.5–272.8°; 270° gives m.p. 273–275°. [i] Gomberg, *Ber.*, **33**, 3147 (1900). [j] Ref. 6. [k] C. S. Marvel, W. H. Rieger and M. B. Mueller, THIS JOURNAL, **61**, 2769 (1939). [l] C. S. Marvel, M. B. Mueller, C. M. Himel and J. F. Kaplan, *ibid.*, **61**, 2771 (1939). [m] C. S. Marvel, J. F. Kaplan and C. M. Himel, *ibid.*, **63**, 1892 (1941).

the great majority of runs it varied between 1×10^{-7} and 3×10^{-7} mhos $cm.^{-1}$.

The electrode bulb volume was calibrated directly with known weights of water with a precision of about one part in one thousand. The cell constant was determined by means of a solution of potassium chloride in conductivity water. The dilution bulb volume was determined directly with water to a precision of two parts in one thousand. It was determined indirectly with potassium iodide and potassium bromide by carrying out regular conductivity runs with these compounds (four dilutions per run) and using Franklin's[14] data for these compounds, in conjunction with the measured specific conductivities and total solution volumes. This method gave a precision of seven parts in one thousand with potassium iodide (one run) and seventeen parts in one thousand with potassium bromide (two runs). Although much less reproducible than the direct method, this procedure yielded an average dilution bulb volume in excellent agreement with that obtained by the direct method. The dilution bulb volume (10.27 ml.) was such that the concentration was reduced to about one-third of its prior value at each dilution.

The compounds measured were obtained either as the chlorides or as the carbinols from various sources. All-glass apparatus was employed in purifying compounds or preparing chlorides from carbinols. Manipulations and apparatus were such as to minimize contact with atmospheric moisture. Samples were stored in weighing bottles in a vacuum desiccator over Drierite or potassium hydroxide.

Compounds obtained as carbinols were converted to the chlorides with acetyl chloride.[15] These chlorides and most of those obtained as such were recrystallized repeatedly from dry C.P. solvents. Useful solvent combinations included acetyl chloride together with benzene or 30–60° petroleum ether or both, benzene–30–60° petroleum ether, carbon tetrachloride–acetyl chloride–30–60° petroleum ether, the same solvents in pairs, and ethyl or butyl acetate–acetyl chloride–30–60° petroleum ether. Samples 2, 4, 6, 10 and 15 (*cf.* Table I) were employed as supplied. The authors wish to express their gratitude to Professor C. S. Marvel, Dr. George B. De La Mater, Dr. William F. Sager and Mrs. Mary Chapman Roha for the compounds which they supplied.

Two of the compounds measured have not been reported previously; the mono-*m*-*t*-butyl derivative of triphenylchloromethane and 9-chloro-9-phenyl-10,10-dimethyl-9,10-dihydroanthracene. The preparations of these are described by De La Mater.[16]

All compounds were white crystalline solids. Hydrolyzable chloride was determined by a semimicro Volhard procedure. Samples (10 to 30 mg.) were dissolved in 5 ml. of nitrobenzene in glass-stoppered flasks. About 3 ml. of water

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[14] E. C. Franklin, *J. Phys. Chem.*, **15**, 675 (1911).

[15] *Org. Syntheses*, **23**, 100 (1943).

[16] G. B. De La Mater, Ph.D. Thesis, Harvard University, 1948, p. 81.

TABLE II

CONDUCTIVITIES AT 0° IN LIQUID SULFUR DIOXIDE

Compound no. (Table I): Concn. mole/liter	1-4[a,b]	5[c]	6[c]	7,8[d]	9,10[e]	11,12[d]	13,14[f]	15[c]
				Λ in Mhos. cm.²/mole				
0.01	16.1			68				
.005	22.3	31	42	81	77	123	130	114
.0025	29.0	42.5	55.5	97	93	136	139.5	130
.001429	37.5	52.5	67.5	111.5	108	146	147	143.5
.001	43.5	60	76	121	118	152	151.5	151.5
.0005	56.5	77.5	96	139	136	161.5	159	165
.00025	73	97.5	117.5	156	151.5	170.5	166	176
.0001429	89	115	134	167.5	162.5	176.5	170	183.5
.0001	100	127	145	173	168.5	180	172	187.5
.00005	123.5	147	161.5	181	176.5	184.5	175	193
.000025	147	165	176	185	180	186	177	197
.00001429	164	176	185.5	186.5	181.5	186.5	178	200
.00001	172	181		187	182	187	178.5	201

[a] Summary of six runs. [b] The data for mono-*p*-deuterotriphenylchloromethane (one run) were indistinguishable from those for triphenylchloromethane. [c] Summary of two runs. [d] Summary of four runs. [e] Summary of five runs. [f] Summary of seven runs.

TABLE III

CONDUCTIVITIES AT −17° IN LIQUID SULFUR DIOXIDE

Concn., mole/liter	Λ in Mhos cm.²/mole Compound no. (Table I) 1-4[a]	13, 14[b]
0.01	24.5	
.005	30.5	112
.0025	40.5	119
.001429	50.5	125
.001	57.5	128.5
.0005	73	134.5
.00025	90	139.5
.0001429	104.5	143
.0001	114	144.5
.00005	131	147
.000025	143.5	149
.00001429	150.5	149.5
.00001	152.5	150

[a] Summary of four runs. [b] Summary of three runs.

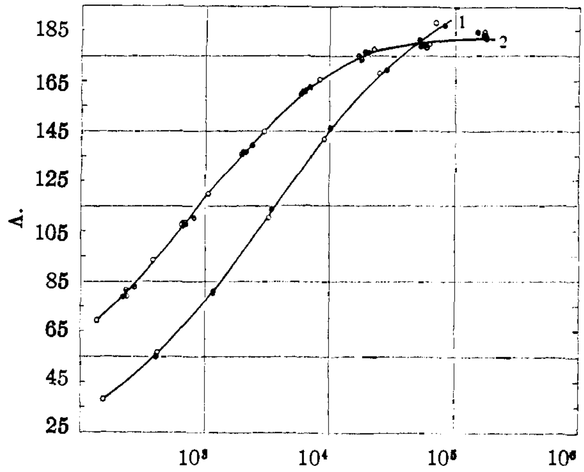

Fig. 2.—Conductivity data: curve 1, mono-*m-t*-butyltriphenylchloromethane: ○ Run 54, ● run 55; curve 2, mono-*p-t*-butyltriphenylchloromethane: ○ run 33, ◓ run 34 (runs done with sample 9, Table I): ◒ run 36, ◐ run 38, ◑ run 45 (runs done with sample 10, Table I).

was added and the mixture shaken for five minutes. The samples were then titrated directly. The analysis was found to have a precision of between 1 and 2%. Melting ranges and analyses are summarized in Table I.

Data

Figure 2 shows typical semilogarithmic plots of equivalent conductance *vs.* dilution for two compounds at 0°. The precision of the data, as estimated by averaging the per cent. deviation of individual points from the smoothed curve for a given compound, is ±2% or better for all compounds.

Tables II and III summarize the equivalent conductance data from the smoothed curves.

Equilibrium constants and limiting conductance values were calculated from the smoothed equivalent conductance data (0.0025 to 0.00001 *M*) by Shedlovsky's method.[8,17] The Shedlovsky equation[8]

$$\frac{1}{\Lambda S(z)} = \frac{1}{K\Lambda_0^2} \times S(z)\Lambda c f_{\pm}^2 + \frac{1}{\Lambda_0}$$

where $S(z)$ is the Shedlovsky function

$$\left[\frac{Z}{2} + \sqrt{1 + \left(\frac{Z}{2}\right)^2}\right]^2$$

K is the equilibrium constant, c is the concentration (moles per liter), and $f_{\pm}$ is the mean ionic activity (evaluated by the Debye–Hückel limiting law), was solved graphically for each compound to yield K and Λ_0 values. The coefficients of the limiting slopes and the Debye–Hückel limiting law were evaluated numerically, employing Birge's 1941 values of the physical constants.[18,19] Thus

$$z = \left[\frac{8.203 \times 10^5\Lambda_0}{(DT)^{3/2}} + \frac{82.43}{(DT)^{1/2}\eta}\right]\Lambda_0^{-3/2}\sqrt{c\Lambda}$$

For liquid sulfur dioxide the dielectric constant, D,

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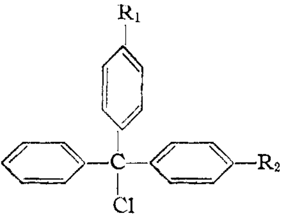
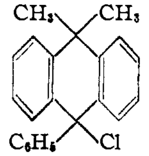
[17] R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

[18] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[19] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2d ed., Reinhold Publishing Corp., New York, N. Y., 1950, pp. 33, 37, 82–83, 186–190.

TABLE IV

SUMMARY OF DATA ON 

Substituent R₁	R₂	R₃	10^5K_{exp} 0°	−17°	ΔF^0, kcal./mole 0°	−17°	Λ_0 mhos cm.²/mole 0°	−17°
H	H	H	4.03	12.0	+5.49	+4.59	208	171
H	H	*m*-CH_3	9.2	....	+5.04	....	201	...
H	H	*m*-*t*-Bu	16.0	....	+4.74	....	201	...
H	H	*p*-CH_3	71	....	+3.93	....	196	...
H	H	*p*-*t*-Bu	76	....	+3.90	....	190	...
H	*p*-*t*-Bu	*p*-*t*-Bu	340	....	+3.08	....	191	...
p-*t*-Bu	*p*-*t*-Bu	*p*-*t*-Bu	800	1000	+2.62	+2.34	182	152
			179	....	+3.43	....	204	...

is 15.6 at 0° and 16.9 at −17°.[20] The viscosity, η, is 0.00394 poise at 0° and 0.00455 poise at −17°.[21,22] Inserting these values, z is $[2.952\ \Lambda_0 + 320.6]\ \Lambda_0^{-3/2}\sqrt{c\Lambda}$ at 0° and equals $[2.882\ \Lambda_0 + 275.4]\Lambda_0^{-3/2}\sqrt{c\Lambda}$ at −17°. Similarly, $\log f_{\pm}$ equals $-6.56\sqrt{c\theta}$ at 0° and $-6.41\ \sqrt{c\theta}$ at −17° for solutions in liquid sulfur dioxide ($\theta = \frac{\Lambda}{\Lambda_0}s(z)$ = degree of dissociation). Values of Λ_0 estimated from the high dilution data were used initially in the calculations. Repetition of the calculations using the limiting equivalent conductances thus found caused only small (1% or less) changes in Λ_0. Plots of the Shedlovsky equation obtained in the second stage of calculation are represented in Figs. 3–5. The constants thus obtained are summarized in Table IV.

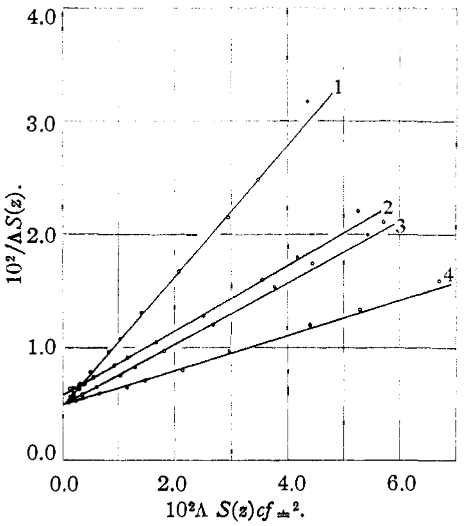


Fig. 3.—Shedlovsky plots for: 1, triphenylchloromethane at 0°; 2, triphenylchloromethane at −17°; 3, mono-*m*-methyl-triphenylchloromethane at 0°; 4, mono-*m*-*t*-butyl-triphenylchloromethane at 0°.

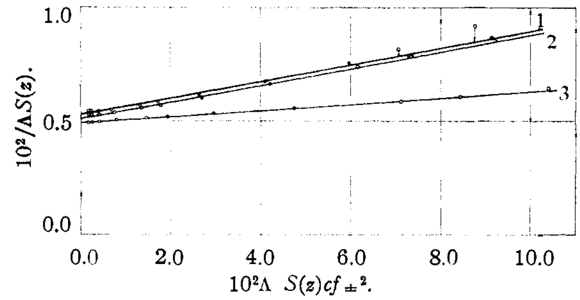


Fig. 4.—Shedlovsky plots for: 1, mono-*p*-*t*-butyltriphenylchloromethane at 0°. 2, mono-*p*-methyltriphenylchloromethane at 0°; 3, 9-phenyl-9-chloro-10-10-dimethyl-9-10-dihydroanthracene at 0°.

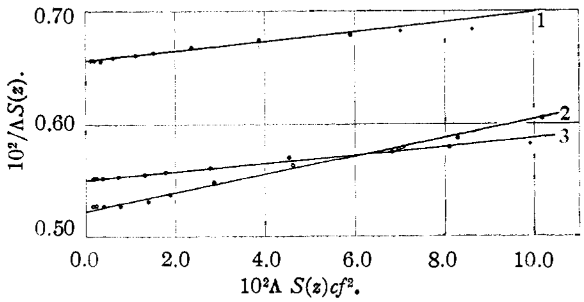


Fig. 5.—Shedlovsky plots for: 1, tris-*p*-*t*-butylphenylchloromethane at −17°; 2, bis-*p*-*t*-butylphenylphenylchloromethane at 0°; 3, tris-*p*-*t*-butylphenylchloromethane at 0°.

Standard heats and entropies of dissociation can be calculated for triphenylchloromethane and its tri-*p*-*t*-butyl derivative using the integrated van't Hoff equation

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[20] "International Critical Tables," Vol. 6, McGraw-Hill Book Co., New York, N. Y., 1929, p. 76.

[21] *Ibid.*, Vol. 7, p. 212.

[22] The value of η at −17° was interpolated from available data but D at this temperature had to be calculated using an extrapolation equation somewhat outside of its stated range of applicability (0–150°).

$$\Delta H^0 = \frac{R \ln (K_1/K_2)}{\dfrac{1}{T_2} - \dfrac{1}{T_1}}$$

if constancy of ΔH° over a 17° range of temperature is assumed. That such an assumption can be only approximate for electrolytes is known.[23] Thus, no significance can be ascribed to small differences in this property. The two compounds, however, have quite different heats of dissociation in liquid sulfur dioxide (Table V).

TABLE V

THERMODYNAMIC CONSTANTS

Compounds	$\Delta F^\circ_{0^\circ}$, kcal./mole	$\Delta H^\circ_{0^\circ}$, kcal./mole	$\Delta S^\circ_{0^\circ}$, e.u.
Triphenylchloromethane	+5.49	−8.9	−53
Tris-*p*-*t*-butylphenylchloromethane	+2.62	−1.8	−17

Discussion

Current theory recognizes three forms of a weak electrolyte which may all be present simultaneously in solution. These are the undissociated molecule, the free ions, and the ionic aggregates held together by purely electrostatic forces. In sulfur dioxide ion pairs are the only such ionic aggregates which need to be considered.[24]

Conductance registers the free ions as opposed to the ion pairs and molecules. The equilibrium constants obtained from conductance data are therefore composites of an ionization constant and a dissociation constant of ion pairs, as shown in the following analysis. For the equilibria

$$\mathrm{RCl} \overset{K_1}{\rightleftarrows} \mathrm{R^+Cl^-} \overset{K_2}{\rightleftarrows} \mathrm{R^+} + \mathrm{Cl^-}$$

the over-all experimental equilibrium constant K_{exp} is expressed by

$$K_{\text{exp}} = \frac{(\mathrm{R^+})(\mathrm{Cl^-})}{(\mathrm{RCl}) + (\mathrm{R^+Cl^-})} = \frac{(\mathrm{R^+})(\mathrm{Cl^-})}{(\mathrm{RCl})(1 + K_1)} = \frac{K_1K_2}{1 + K_1}$$

and

$$K_1 = \frac{K_{\text{exp}}}{K_2 - K_{\text{exp}}}$$

Of the equilibrium constants for the two steps, K_1 should be increased by any factors which stabilize the ions relative to the covalent molecule, while K_2 should be influenced by structural changes only through their effects upon the "distance of closest approach" of the cation.[25,26] Thus although our constants cannot be directly identified with K_1K_2 or K_2, the manner in which they change with structure can afford some indication as to the essential nature of the equilibrium involved. The "distance of closest approach" is closely related to the actual ionic dimensions for the tetraalkylammonium ions, which are approximately spherical.[27] The variation of degree of ion pair dissociation with change in ionic dimensions for such ions can be inferred from the work of Tucker and Kraus[28] who found, for instance, that in ethylene chloride at 25° ($D = 10.23$) for tetramethylammonium picrate $K_{\text{dissn}} \times 10^4 = 0.32$, for the tetraethyl compound 1.59 and for tetra-*n*-amylammonium picrate 2.38. Except for the first member of the series, K_{dissn} varies very gradually with variation in ionic dimensions. Triphenylcarbonium ion and its derivatives and analogs are, however, planar or, more likely, shaped like a flat pinwheel.[29] Furthermore, the positive charge on such an ion is distributed and is not concentrated at any one atom. The effective distance of closest approach of a spherical anion ($\mathrm{Cl^-}$) to such a cation must vary very little with meta and para substitution. Unfortunately, no mathematical treatment appears to have been carried out for the ion pair interaction of a disk-shaped ion with a spherical one. It, nevertheless, seems entirely probable that for these ions the extent of ion pair association should be very insensitive to small variations in the diameter of the disk.

Ziegler and Wollschitt,[4] on the basis of their finding that plots of Λ/Λ_0 *vs.* concentration for trityl perchlorate and several of its para methyl and methoxyl derivatives were identical, concluded that these compounds were strong electrolytes, *i.e.*, completely ionized. From the congruence of these curves (insofar as the accuracy of the data permits) it can be further concluded that the dissociation constants for ion pairs derived from these compounds are identical. Thus, for perchlorates, K_2 is quite constant over a range of structural variation somewhat smaller than that encountered in the present work. It seems quite reasonable that the same should be true for the chlorides.

The assumption of approximate constancy of K_2 over the whole range of compounds thus appears to be quite sound. On this basis, a lower limit for K_2 is easily established. K_2 for all the compounds must be at least as large as K_{exp} for the tri-*p*-*t*-butyl compound. Thus, for the first five compounds in Table IV, K_2 is at least ten times as big as K_{exp}. The difference $K_2 - K_{\text{exp}}$ will therefore change but little with changing K_{exp}. For these compounds, differences in K_{exp} directly reflect differences in K_1. Comparison of 10,10-dimethyl-9-phenyl-9-chloro-9,10-dihydroanthracene with members of the triphenylchloromethane series (as to K_1) is less certain because of the possibility that, with the change in molecular shape, K_2 may vary somewhat. Discussing the effect upon K_1 of stepwise introduction of para alkyl groups is complicated by the fact that the di- and trisubstituted compounds are such strong electrolytes that $K_2 - K_{\text{exp}}$ probably changes appreciably in going from one to the other. From the relationship among K_{exp}, K_1 and K_2, it can, however, be deduced that K_{exp} will increase less rapidly than K_1 and that the observed relative changes in K_{exp} must be less than those in K_1.

For the first five compounds of Table IV the experimental dissociation constants are a measure of the stabilities of the corresponding carbonium ions relative to some molecular species with much more covalent character than an ion pair and presumably identical with or similar to the triarylmethyl compounds in non-ionizing solvents.

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[23] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, pp. 313–314.

[24] Ref. 19, p. 193.

[25] N. Bjerrum, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **7**, No. 9, 1 (1926); *C. A.*, **22**, 1263 (1928).

[26] Ref. 19, pp. 42–45.

[27] C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933).

[28] L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947).

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

Although it is well recognized that alkyl groups have an "electron releasing" effect toward the benzene ring, the mechanism of this effect is not convincingly represented by classical electronic theory. Direct comparison of the dipole moments of toluene (0.37 *D*) and *t*-butylbenzene (0.70 *D*) suggests that the electron-releasing effect of the *t*-butyl group is greater than that of methyl.[30] The rates of certain ionization and displacement reactions[31,32] and of the nuclear halogenation of alkylbenzenes,[33,34] and the wave lengths and intensities of certain absorption bands of the alkylbenzenes in the near ultraviolet,[35] reveal a small contrary effect, which is commonly described in terms of "hyperconjugation" or resonance involving electrovalent C–H bonds.[36] The generalization has been made that the Baker–Nathan order of groups appears in excited states of the molecule, while the "inductive" effect appears in measurements relating to the ground state. However, the para-substituted benzoic acids from *p*-toluic to *p*-*t*-butylbenzoic do not fall in either smooth order with respect to their ionization constants,[37] although the quantity measured is an equilibrium between the ground state of the acid and those of the ions.

The present work reveals one highly significant point in the comparison between the methyl and the *t*-butyl group. The introduction of either of these groups into the meta position in triphenylchloromethane is favorable to the ionization, but the *t*-butyl group substantially more so than the methyl group. The *t*-butyl therefore excels the methyl group in the property of general electron release which can be felt at the meta position. When the methyl and *t*-butyl groups are compared in the para position, the effect of each is much larger than in the meta, and the difference between the two groups has become negligible. These observations are entirely consistent with the often expressed view that the *t*-butyl group has a higher "inductive" effect than the methyl, but a lower "hyperconjugative" effect. To make this interpretation consistent, however, these statements must be supplemented by the recognition[38,39] that the general inductive effect of a group is not, as often supposed, transmitted preferentially to the ortho and para positions by a resonance mechanism within the ring, but falls off from position 1 to position 4 in a manner suggesting a simple coulombic interaction.

The substantial difference between the relative effects of the methyl and *t*-butyl groups in the meta and para positions where an equilibrium constant is being measured indicates two things: (1) these two groups differ more largely in their inductive and hyperconjugative effects than is usually apparent from a series of measurements reflecting the resultant of the two effects; and (2) both effects are important in the ground state, as shown by their influence in the present equilibrium system.

Perhaps the best description of the origin of the general inductive effect is that given by Walsh[40] in terms of continuously varying hybridization of bonding orbitals. According to this scheme the high inductive effect of the *t*-butyl group is cognate with the stability of the trimethylcarbonium ion,[41] and is associated with increased *s* character in the CH_3–C bonds and hence increased *p* character in the orbital of the central carbon of the *t*-butyl group which bonds it to the benzene ring. Since all bonds from a carbon atom of benzene to a side chain occupy sp^2 orbitals of the ring carbon, this produces a polarized bond with its negative end toward the ring.

In contrast with the behavior of carbonium ions the triphenylmethyl free radical is stabilized more by introduction of a meta methyl group than by a para methyl group, and in both positions *t*-butyl is substantially more effective than methyl.[42]

On consideration of the results of stepwise introduction of *p*-*t*-butyl groups it is found that the introduction of the first such group increases dissociation by a much larger factor than does the second while the third causes an even smaller relative increase. As previously pointed out, the factors by which K_1 changes in going from the mono- to the disubstituted compound and from the di- to the trisubstituted compound are probably increasingly greater than those for K_{exp}. Thus, the three factors would be less different in terms of K_1 than for K_{exp}. These results contrast strongly with the free radical case. Tetraphenyl-di-*p*-tolylethane and diphenyltetra-*p*-tolylethane have very similar dissociation constants, both about five times that for hexaphenylethane. $K_{\text{dissn.}}$ for hexa-*p*-tolylethane is about ten times larger than that for the di- and tetrasubstituted compounds.[43]

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(30) J. W. Baker and L. G. Groves, *J. Chem. Soc.*, 1144 (1939).

(31) J. W. Baker and W. S. Nathan, *ibid.*, 1840 (1935).

(32) E. D. Hughes, C. K. Ingold and N. A. Taber, *ibid.*, 949 (1940).

(33) P. B. D. de la Mare and P. W. Robertson, *ibid.*, 279 (1943).

(34) E. Berliner and F. J. Bondhus, THIS JOURNAL, **68**, 2355 (1946).

(35) F. A. Matsen, W. W. Robertson and R. L. Chuoke, *Chem. Revs.*, **41**, 273 (1947).

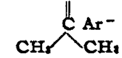
(36) The term "hypoerconjugation" has been widely adopted and used to embrace all forms of no-bond resonance including the Baker–Nathan effect. However, the molecular-orbital discussions attending the introduction of the term "hyperconjugation" [R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941)] have had nothing to say about the relative importance of electrovalent bond character in the C–H bond and the C–C bond. Indeed, one would not anticipate on the basis of these quantum mechanical treatments any obvious difference between the hyperconjugation in toluene and that in *t*-butylbenzene.

(37) J. W. Baker, J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 1774 (1937).

(38) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

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

(40) A. D. Walsh, *Discussions of the Faraday Soc.*, **2**, 18 (1947).

(41) The "inductive" effect transmitted by the *t*-butyl group is thus contributed to by hyperconjugation of the type  $\mathrm{H}^{+}\mathrm{CH}_3{=}\mathrm{C}(\mathrm{CH}_3)_2\ \mathrm{Ar}^{-}$. This need not confuse the distinction between this total effect and the one originating in hyperconjugation with double-bond character between the α-carbon atom and the ring. For an example of still greater complexities in the discussion of hyperconjugation, see E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949).

(42) C. S. Marvel, J. F. Kaplan and C. M. Himel, *ibid.*, **63**, 1892 (1941).

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