erties of *trans*-2,3-dihalogenotetralin are very similar to those of *trans*-4,5-dihalogeno-1-cyclohexene. (3) As to *trans*-1,2-dihalogenotetralin, probably because of the sterical repulsions of halogen at C-1 with C-8 and H at C-8, the *ee* conformation become more unstable than that of the 2,3-isomer, therefore, ΔE becomes larger than that of 2,3-dihalogenotetralin.

From these conclusions the following could be speculated: (1) In regard to *ac*-monosubstituted positional isomers, the abundance ratio of *axial* conformation to *equatorial* one may become larger in α-substituted tetralin than in the β-substituted one. (2) In 1,2-disubstituted tetralin, not only of *trans* configuration but of *cis* configuration, the more stable conformation may be generally the one in which the substituent at C-1 is *axial.* When two substituents are fused together to make another ring, the *trans* configuration cannot occur other than in 1*e*2*e;* in the *cis* configuration, however, 1*a*2*e* may be more stable than 1*e*2*a*.

Acknowledgment.—The author wishes to express his sincere thanks to Professor Tetsuo Mitsui for his invaluable encouragement, to Professor Yonezo Morino and Dr. Ichiro Miyagawa of Tokyo University and Dr. Kiyoshi Sakashita of Tokyo Institute of Technology for their constant guidance and advice, rendered during the course of this work, and to Mr. Ichiro Taniguchi of the Department of Electronical Engineering of Kyoto University for his assistance in preparing the measuring apparatus.

KYOTO, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY]

Ionization and Dissociation Equilibria in Liquid Sulfur Dioxide. VI. Hexaphenylethane[1]

BY HARRY P. LEFTIN AND NORMAN N. LICHTIN

RECEIVED OCTOBER 4, 1956

The effects of solute purity, light and oxygen on the electrical conductivity of sulfur dioxide solutions of hexaphenylethane have been investigated. Contrary to previous reports, pure solutions of hexaphenylethane do not conduct significantly. Electrolytes are, however, generated by the action of light and of oxygen. Comparison of the data for oxygenated solutions of hexaphenylethane with the conductivity of tetramethylammonium sulfate in liquid sulfur dioxide at 0.1° over the dilution range 200 to 100,000 liters per mole suggests that a 2–1 electrolyte is present. These observations make possible simple explanation of earlier reports on the properties of solutions of hexaarylethanes in sulfur dioxide.

Introduction

The differences in behavior of solutions of hexaphenylethane[2] in sulfur dioxide and in organic solvents has been the subject of considerable discussion. Thus in so called "non-ionizing" solvents, molecular weight,[3] magnetic susceptibility[4] and spectral[5] data in conjunction with photochemical instability[6] and rapid reaction with oxygen[7] demonstrate conclusively the dissociation of hexaarylethanes into free radicals. In sulfur dioxide, however, the solutions have been reported to conduct the electric current,[8] to be photochemically stable[9] and to fail to react with oxygen.[10] Moreover, the observed color[11] and spectrum[12] in SO_2 have been described as differing markedly from those observed in many other solvents.[13]

This anomalous behavior has received several chemical interpretations[14] which differ in detail but which all assume an ionization mechanism involving only hexaphenylethane and sulfur dioxide. These proposed mechanisms can be divided into two general classes depending upon the valence type of the electrolyte produced and, therefore, in view of the recent demonstration[15] of the applicability of modern electrolyte theory to solutions of electrolytes in sulfur dioxide, would be distinguishable on the basis of conductivity data alone. Unfortunately the data of Walden[8a] and of Gomberg[8b] lack precision and do not extend over a sufficient concentration range to be useful for this purpose. Accordingly, attempts were made initially to obtain precise conductivity data employing crystalline samples of pure hexaphenylethane. These investigations revealed[16] that the observed conductivity is an artifact of interaction with light or oxygen and is not characteristic of pure solutions.

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(1) Based on a dissertation submitted by H. P. Leftin in partial fulfillment of a requirement for the Ph.D. at Boston University, May, 1955.

(2) For general reviews of this subject see: (a) M. Gomberg, *Chem. Revs.*, **1**, 91 (1924); (b) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 680–713.

(3) (a) M. Gomberg and L. H. Cone, *Ber.*, **37**, 2037 (1904); (b) M. Gomberg and C. S. Schoepfle, THIS JOURNAL, **39**, 1652 (1917).

(4) (a) N. W. Taylor, *ibid.*, **48**, 854 (1926); (b) E. Muller, I. Muller-Radloff and W. Bunge, *Ann.*, **520**, 235 (1935); (c) M. F. Roy and C. S. Marvel, THIS JOURNAL, **59**, 2622 (1937); (d) R. Preckel and P. W. Selwood, *ibid.*, **63**, 3397 (1941).

(5) (a) J. Piccard, *Ann.*, **381**, 347 (1911); (b) K. Ziegler and L. Ewald, *ibid.*, **473**, 163 (1929).

(6) S. T. Bowden and W. J. Jones, *J. Chem. Soc.*, 1149 (1928).

(7) (a) M. Gomberg, *Ber.*, **33**, 3150 (1900); THIS JOURNAL, **22**, 757 (1900); (b) J. Schmidlin, *Ber.*, **41**, 2471 (1908).

(8) (a) P. Walden, *Z. physik. Chem.*, **43**, 443 (1903); (b) M. Gomberg and L. H. Cone, *Ber.*, **37**, 2033 (1904); **38**, 1342 (1905); (c) M. Gomberg and F. W. Sullivan, Jr., THIS JOURNAL, **44**, 1810 (1922).

(9) Reference 6, p. 1153.

(10) L. C. Anderson, THIS JOURNAL, **57**, 1673 (1935).

(11) M. Gomberg and F. W. Sullivan, *ibid.*, **44**, 1829 (1922).

(12) (a) K. H. Meyer and H. Wieland, *Ber.*, **44**, 2557 (1911); (b) Reference 10.

(13) Ziegler and Ewald, reference 5b, reported that the spectra of hexaphenylethane solutions are identical in a series of solvents covering a wide range of dielectric constant, ion solvating power and structural properties.

(14) (a) Reference 2a, p. 102; (b) P. Walden, "Chemie der Freien Radicale," S. Hirzel, Leipzig, 1924, p 154; (c) W. A. Waters, "Chemistry of Free Radicals," Oxford Press, London, 1948, pp. 35–36; (d) Reference 2b, p. 712; (e) H. I. Cole, *Philippine J. Sci.*, **19**, 681 (1922); (f) G. Cilento and W. F. Walter, THIS JOURNAL, **76**, 4469 (1954).

(15) (a) N. N. Lichtin and P. D. Bartlett, *ibid.*, **73**, 5530 (1951); (b) N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 160, 164 (1956).

(16) H. P. Leftin and N. N. Lichtin, THIS JOURNAL, **76**, 2593 (1954).

Experimental

Hexaphenylethane.—This was prepared in an all-glass apparatus by shaking a solution of 30 g. (0.108 mole) of triphenylchloromethane in 300 ml. of acetone with 80 g. (0.40 mole) of mercury. The reaction was carried out in a 580-ml. sealed flask, A, shielded from light by wrapping with aluminum foil and equipped with a side arm closed by a fragile glass membrane. Prior to sealing, the reaction flask and contents were cooled to −40° and evacuated to the autogenous pressure of the mixture. Shaking was provided at room temperature by a Burrell model CC shaker set at speed 10. After a 9-hour shaking period the side arm (containing a sealed in coarse sintered disk) of a receiving flask, B, was sealed onto the side arm of the reaction flask. The receiving flask was then dried by flaming and pumping and finally evacuated to a pressure of 10^{-4} mm. through a stopcock, C, sealed to its neck. With the stopcock closed, the apparatus was removed from the vacuum line and transferred to a darkened room where the synthesis was completed. The fragile glass membrane was smashed by means of a glass bead and the orange solution was filtered through the coarse sintered disk by rotating the apparatus. A small side bulb on flask A served to prevent plugging of the filter disk by trapping most of the mercury residue. This residue was washed free of product with solvent distilled back into A from B. During such distillations the solutions were never warmed above 30° and the process was speeded by cooling the receiving bulb to −78°. The product was crystallized by concentrating the solution to one-fourth of its original volume and cooling in an ice-bath for several hours. The mother liquors were decanted into vessel A, and the product then recrystallized from solvent freshly distilled from A into B. Usually three recrystallizations were executed prior to final product isolation. Following the removal of mother liquors from the final recrystallization the apparatus was dismembered by sealing off at the connecting arm.

The vessel containing the yellow or buff colored crystalline product was wrapped with aluminum foil and pumped through C for 24 hours at a pressure of 10^{-5} mm. It was next sealed off from the vacuum line directly below C and transferred to a vacuum dry-box.[17] The dry-box was evacuated overnight to a pressure of 10^{-3} mm. and filled with "Seaford"[18] nitrogen which had been passed over fine copper turnings at 800°, cooled to −78° and finally passed over Drierite. The dry-box atmosphere was further purified by exposure to sodium until a freshly cut surface of the metal showed no signs of tarnish after two hours. Light entering the dry-box was kept to a minimum with the aid of a red filter fashioned from a watch glass made of Corning L. A. glass.

After the flask was opened in the dry-box the yellow solid was transferred to a sintered glass funnel and washed rapidly with a small quantity of pure acetone. This simple washing procedure effectively removes all of the colored surface impurity[19] leaving pure white crystalline hexaphenylethane. The pure product was next distributed into glass bulbs for analysis, conductivity measurement (*vide infra*) and melting point determination. In this way several samples of identical history could be obtained.

Several batches of hexaphenylethane were prepared by this method and one batch was prepared by the method of Lichtin and Thomas.[20]

At least two samples or each lot of hexaphenylethane were transferred to bulbs and analyzed by quantitative oxygenation in the absence of pyrogallol according to the procedure of Lichtin and Thomas.[20] Melting point capillary tubes were filled in the dry-box, temporarily sealed with a plug of Apiezon "Q" putty, removed from the dry-box and immediately sealed with a needle point flame. Melting points were determined using an electrically heated stirred H type bath and were not corrected. Table I summarizes the relevant data for different batches.

TABLE I

PHYSICAL PROPERTIES OF HEXAPHENYLETHANE

Color	Melting range,[a] °C.	Oxygen absorption (% of theory)
White	153.5–154	99.5 ± 0.1
White	153–154	97.2 ± .1
Pale yellow	.....	95.8 ± .3
Pale yellow	146–148	94.0 ± .1
Yellow	144–146	90.4 ± .3

[a] Literature values: 145–147°, M. Gomberg, THIS JOURNAL, **36**, 1144 (1914); 150–152° (cor.) ref. 20.

Reagents and Solvents.—Triphenylchloromethane was prepared from Eastman White Label triphenylcarbinol by reaction with acetyl chloride in dry ether. A pure white product was obtained by rapid crystallization from a hot saturated solution. Recrystallization from ether and vacuum drying at room temperature afforded 93 to 97% yields of pure white crystalline product, m.p. 112.5–113° (uncor.).

Mercury was triple distilled C.P. grade and was outgassed at 100° for several minutes before use. The following solvents were of C.P. grade: acetone was stored over Drierite for several weeks, filtered, refluxed over calcium hydride and distilled before use; ether was dried over calcium hydride and filtered.

Sampling Technique for Conductivity Runs.—Samples (50–200 mg.) for conductivity measurements were stored in sealed preweighed break-off type bulbs (equipped with female standard taper joints) which were filled in the vacuum dry-box. The filled bulbs were then attached to a manifold, which was then evacuated by means of an external pump connected through the base plate of the dry-box. The evacuated manifold and bulbs were transferred from the dry-box to a vacuum line and pumped at 10^{-5} mm. for several hours. The sample bulbs were then sealed off at their necks. During the sealing operation the lower portion of the bulb containing the sample was kept immersed in an ice-bath in order to prevent thermal decomposition.

Sample weights (usually 50–200 mg.) were determined by difference with an accuracy of better than ±1 mg. An appropriate vacuum correction, based on the measured bulb volume, was applied in each case and was usually of the order of 3–4 mg. with an uncertainty of about 0.5 mg. due to the volume occupied by the sample. The bulbs were wrapped in aluminum foil and stored in a light-proof box in the freezing compartment of a refrigerator. Samples stored in this manner showed no visible evidence of deterioration after 18 months.

Conductivity Measurements.—The conductivity cell, thermostat and bridge assembly employed in this work have been described previously.[21] The temperature of measurement was −8.93 ± 0.03°. The vacuum line was similar to that used in earlier work.[21] Procedures employed in preparing solutions in the cell differed from those previously reported in the following respects.

Hexaphenylethane was introduced into the conductivity cell by smashing the breakoff diaphragm of an evacuated sample bulb sealed to the inlet tube of the sealed, evacuated, sulfur dioxide-filled cell. A glass grid was installed in the inlet tube in order to support the glass-sheathed, gold-plated, solenoid-activated, iron rod used for this purpose. That this grid did not introduce significant drainage errors was established by measurements employing triphenylchloromethane as solute. The small quantity of glass fragments introduced into the electrode compartment by this procedure caused a negligible error in the measured volume of the solution. All conductivity measurements as well as the preparation of the solutions were carried out under dark-room conditions except where otherwise indicated. Only light provided by a Kodak ruby-red safelight was permitted

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(17) G. R. Thomas and N. N. Lichtin, *Rev. Sci. Inst.*, **23**, 738 (1952).

(18) Containing 1% hydrogen, supplied by Air Reduction Co.

(19) Gomberg[2a] claimed that even in the solid state hexaphenylethane undergoes a slow photochemical transformation. Since light of the wave length most active in effecting this transformation[12] was rigorously excluded in the present procedures, it seems unlikely that the surface color is due to this cause. The ease with which the color can be removed suggests that it may be due to adsorption of a soluble colored impurity or of the monomeric radical from the mother liquors. In this respect it is interesting that color was not produced when white hexaphenylethane in an evacuated sealed tube was exposed either to sunlight or to ultraviolet light for several days at room temperature. In the absence of light, however, a yellow coloration developed when the ethane was exposed to the atmosphere.

(20) N. N. Lichtin and G. R. Thomas, THIS JOURNAL, **76**, 3021 (1954).

(21) N. N. Lichtin and H. Glazer, *ibid.*, **73**, 5537 (1951).

to contact the solutions. Sulfur dioxide, Virginia Smelting Co., Extra-Dry Es-O-Too refrigeration grade, was dried in the gas phase over $Mg(ClO_4)_2$ and distilled into the cell from a helix-packed bulb. In about half of the runs the solvent was degassed prior to distillation into the cell by pumping at −78° for varying periods of time. In two runs the degassed solvent was further purified by distillation from about 2 g. of hexaphenylethane. Solvent conductivity determined at the end of each run was usually in the range 1.0×10^{-7} to 2.2×10^{-7} mho cm.$^{-1}$.

Sulfur dioxide solutions of the product formed by the reaction of hexaphenylethane with oxygen were prepared by the following procedure. A stopcock was added to the exit arm of the cell. The cell was filled with degassed sulfur dioxide, removed from the line and a solution of hexaphenylethane prepared in the usual way. The solution was then thermostated, its resistance measured, and dry tank oxygen admitted through the stopcock with the aid of the vacuum line. Equilibration with oxygen was considered complete when the conductivity of the solution remained unchanged for two hours. The cell was then evacuated to the autogenous pressure of the solution at −35°, sealed off at the stopcock and conductivity behavior measured at −8.9° in the usual way. After several dilutions these runs had to be terminated because the residue was so strongly solvated that a sufficient volume of solvent could not be recovered by distillation from the reservoir bulb.

Experiments in which the influence of light was examined were carried out at 0° using an unsilvered Dewar ice thermostat. Illumination of the electrode compartment of the cell was provided by a Burton long wave length ultraviolet lamp.

Recovery of Solutions.—The design of the conductivity cell did not permit recovery of solutes after a conductivity run without atmospheric contamination. Therefore, solutions for this purpose were prepared with the aid of the vacuum line in a separate reaction vessel. A solution of hexaphenylethane (99.5% purity by oxygenation) in degassed sulfur dioxide was maintained in the dark at about −10° for four hours. Removal of the solvent under reduced pressure left a bright yellow residue which was pumped at 10^{-5} mm. for 24 hours. This residue, dissolved in acetone, showed the presence of unchanged hexaphenylethane by a positive Schmidlin test[22] and by the formation of triphenylmethyl peroxide (m.p. 185–186°) on exposure to oxygen.

The addition of oxygen to a solution of the ethane in degassed sulfur dioxide in the dark afforded a blood-red residue which failed to satisfy Schmidlin's criterion and did not yield any ditrityl peroxide. The color of the residue changed to a dirty brown on exposure to atmospheric moisture. The residue was insoluble in hydrocarbon solvents, chloroform and carbontetrachloride. Yellow solutions were obtained in methanol, ethanol, acetone, ether and glacial acetic acid. However, attempted crystallization from these solvents afforded only intractable gums. Hydrolysis of an acetone solution gave an almost white, gummy precipitate which could not be crystallized. This hydrolysis product behaved like a triarylcarbinol in Bowden's[23] test. Its visible spectrum in 98% sulfuric acid solution was similar but not identical to that of triphenylcarbinol. An intense absorption band with its maximum at 440 mμ and a shoulder at 410 mμ was observed with the hydrolyzate, whereas triphenylcarbinol displays maximum absorption at 435 mμ with an only slightly less intense maximum at 410 mμ. Since the hydrolyzate was impure these data can only be regarded as suggestive. The aqueous filtrate from the hydrolysis did not show the presence of sulfate ion when tested with barium chloride.

Triphenylmethyl Peroxide.—This was prepared by oxygenation of hexaphenylethane in benzene solution in the dark. Recrystallization from chloroform afforded white crystals, m.r. 186–187°. This material (3.4 mg.) ground to a fine powder failed to dissolve completely in degassed liquid SO_2 (45 ml.) even after standing at 0° for three hours with occasional mixing. Contrary to Walden's[8a] observations, the solution remained colorless and its specific conductivity (3×10^{-7} mho cm.$^{-1}$ compared to 1×10^{-7} for the pure solvent) remained constant. These results establish that trityl peroxide, present as an impurity in hexaphenylethane, cannot account for the observed conductivity of sulfur dioxide solutions of the parent hydrocarbon.

Tetramethylammonium Sulfate.—This was prepared by shaking for 24 hours a solution of 19 g. (0.12 mole) of Eastman White Label tetramethylammonium bromide in 50 ml. of distilled water with 15 g. (0.06 mole) of C.P. silver sulfate at room temperature in the absence of light. The silver bromide was removed and the solution treated for three 10-hour periods with fresh batches (10 g.) of silver sulfate until no further reaction could be detected. The solution was carefully evaporated to dryness on a steam-bath and the residue was dissolved in 95% ethanol, filtered, and crystallized by adding acetone. The product, recrystallized three times from an acetone–alcohol mixture, washed with acetone, pulverized and dried over P_2O_5 for two weeks, was a white, hygroscopic powder. Its purity by gravimetric sulfate analysis was 99.4 ± 0.1%.

Results and Discussion

Data.—The conductivity of a solution of hexaphenylethane in liquid sulfur dioxide purified only by passage through $Mg(ClO_4)_2$ and distillation increases significantly under the influence of ordinary fluorescent tube room illumination or daylight. Under dark-room conditions the conductivity of such a solution does not change with time. Measurements performed in the dark are, however, not reproducible from sample to sample even when carried out on samples of high purity and identical history. Yet, though the Λ *vs.* v curves are quite different, they resemble each other in a way which suggests that the same electrolyte is present in all cases but at concentrations which deviate from the stoichiometric values by factors that differ from run to run. This is illustrated in Fig. 1. Included for comparison are plots of the data for typical 2:1 and 1:1 electrolytes, tetramethylammonium sulfate and bromide, respectively. The former, but not the latter, resembles the hexaphenylethane curves.

The data of Table II illustrate the effect on the conductivity of solutions of purification of the solvent. Evidently, conductivity is associated with the presence of a volatile impurity which can be removed efficiently by preliminary treatment with hexaphenylethane. These facts, combined

TABLE II

EFFECT OF SOLVENT PRETREATMENT ON CONDUCTIVITY AT −8.9° OF HEXAPHENYLETHANE SOLUTIONS PREPARED IN THE DARK

Solute purity,[a] %	Dilution, l./mole	$\kappa \times 10^6$,[b] mhos cm.$^{-1}$	Solvent pretreatment
95.8	208.1	70.4	No degassing
94	219.2	9.86	Pumped 1 hr.
94	236.3	2.67	Pumped 4 hr.
97	226.2	0.95	Pumped 3 hr., redistilled from Ph_6C_2
97	111.7	3.77	Pumped 2 hr.
97	111.7	362.1	Above soln. after treatment with O_2
97	250	206	Above soln., diluted

[a] By quantitative oxygenation. [b] Corrected for solvent conductance.

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[22] A solution of hexaphenylethane in an organic solvent loses its yellow color instantly when agitated in the presence of air. The color returns slowly when the solution is then allowed to stand undisturbed. This phenomenon, first described by Schmidlin[7b], can be repeated several times until all of the hexaphenylethane has been converted to the peroxide.

[23] S. T. Bowden, *Analyst*, **59**, 618 (1934). An intense color characteristic of a triarylcarbonium ion is produced when a triarylcarbinol dissolved in ether is treated first with a drop of concentrated HCl and then with a saturated ether solution of zinc chloride.

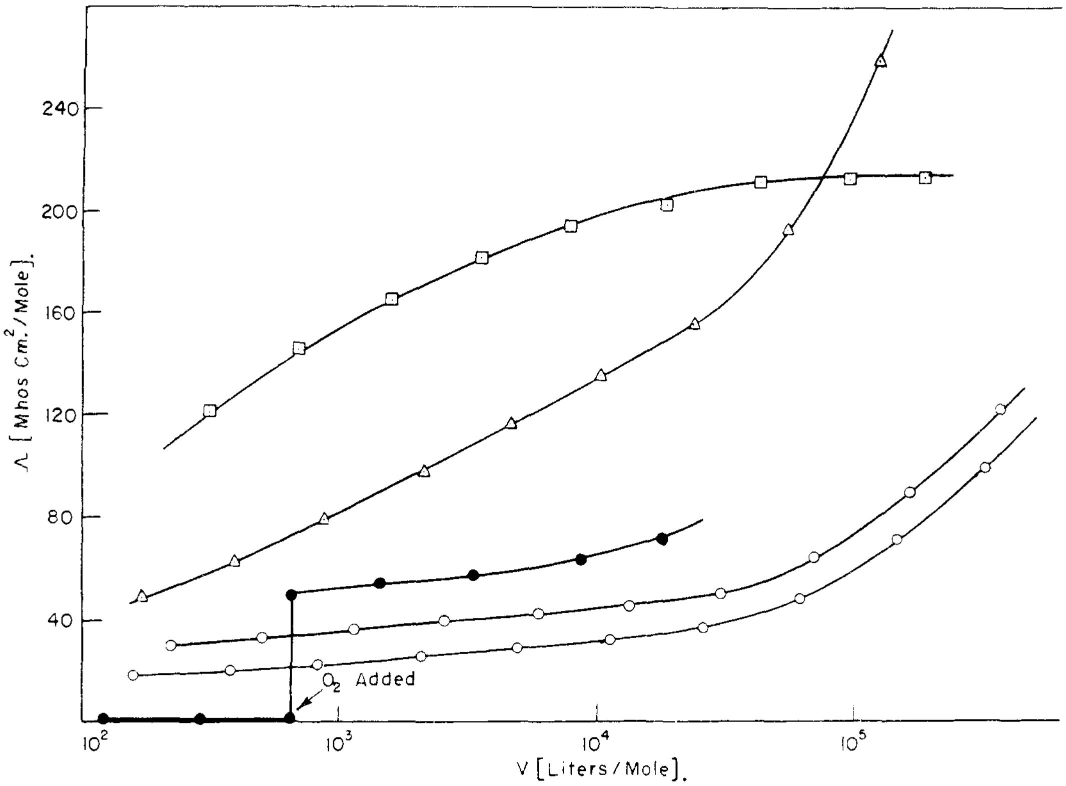

Fig. 1.—Conductivity data in sulfur dioxide solution: —○—, hexaphenylethane (99.5% by O_2 analysis) in ordinary SO_2 (containing O_2 as impurity) at $-8.9°$; —●—, hexaphenylethane (99.5% by O_2 analysis) in degassed SO_2 at $-8.9°$, data to the right of the arrow indicate behavior after the addition of O_2; —△—, tetramethylammonium sulfate at 0.1° (typical 1-2 electrolyte); —□—, tetramethylammonium bromide at $-8.9°$ (typical 1-1 electrolyte).

with the very large increase in conductivity consequent upon addition of oxygen to a feebly conducting degassed solution, lead to the conclusion that this impurity is molecular oxygen. Other facts support this conclusion.

The conductivity achieved on saturating with oxygen is greater than that observed for solutions prepared without degassing (*cf.* Fig. 1) although of the same order of magnitude. As detailed in the Experimental section, hexaphenylethane can be recovered, apparently unchanged, from solution in degassed sulfur dioxide, but the residue remaining after removal of solvent from an oxygenated solution is neither hexaphenylethane nor its peroxide. Ditrityl peroxide is, in fact, only slightly soluble in sulfur dioxide and its saturated solutions do not conduct significantly. The oxygenation of hexaphenylethane in sulfur dioxide is irreversible, however, as demonstrated by the use of hexaphenylethane as a getter from which purified sulfur dioxide can be distilled and by the fact that thorough degassing of an oxygenated solution does not affect its conductivity materially. Solutions resulting from oxygenation are similar in appearance (blood-red) to these prepared in sulfur dioxide which has not been degassed. Solutions in degassed sulfur dioxide are yellow and visually appear to be identical with solutions of hexaphenylethane in common organic solvents.

The action of near ultraviolet light on the conductivity of a solution of hexaphenylethane in degassed sulfur dioxide and of an oxygenated solution is illustrated in Fig. 2. Degassed solutions are strongly and irreversibly affected while oxygenated solutions appear to be inert. Irradiation of solutions in degassed sulfur dioxide produces a change in color from yellow to brown. Removal of solvent from such irradiated solutions yields a dark red gum which responds negatively to tests for the presence of hexaphenylethane.

Information on the nature of the oxygenation product is, at present, fragmentary and inconclusive. Observations on the product of hydrolysis of the oxygenation product suggest the presence of impure triphenylcarbinol. This is supported by the spectroscopic observations reported for solutions in sulfur dioxide which very probably contained the oxygenation product as the principal solute. That the anion probably bears a charge of minus two is indicated by the comparisons of Fig. 1. The same conclusion follows from the application of Shedlovsky's procedure[24] for determining equilibrium constants to the data of a typical run with hexaphenylethane in ordinary sulfur dioxide and to the data for tetramethylammonium sulfate on the basis of the assumption that *both solutes are 1:1 electrolytes*. Relevant conductivity data are summarized in Table III. The resulting similar strongly inflected plots of $1/\Lambda S(z)$ *vs.* $c\Lambda f_{\pm}{}^2S(z)$[25] are

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(24) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(25) $S(z)$ is Shedlovsky's function, c the concentration in moles per liter and $f_{\pm}$ the mean ionic activity coefficient.

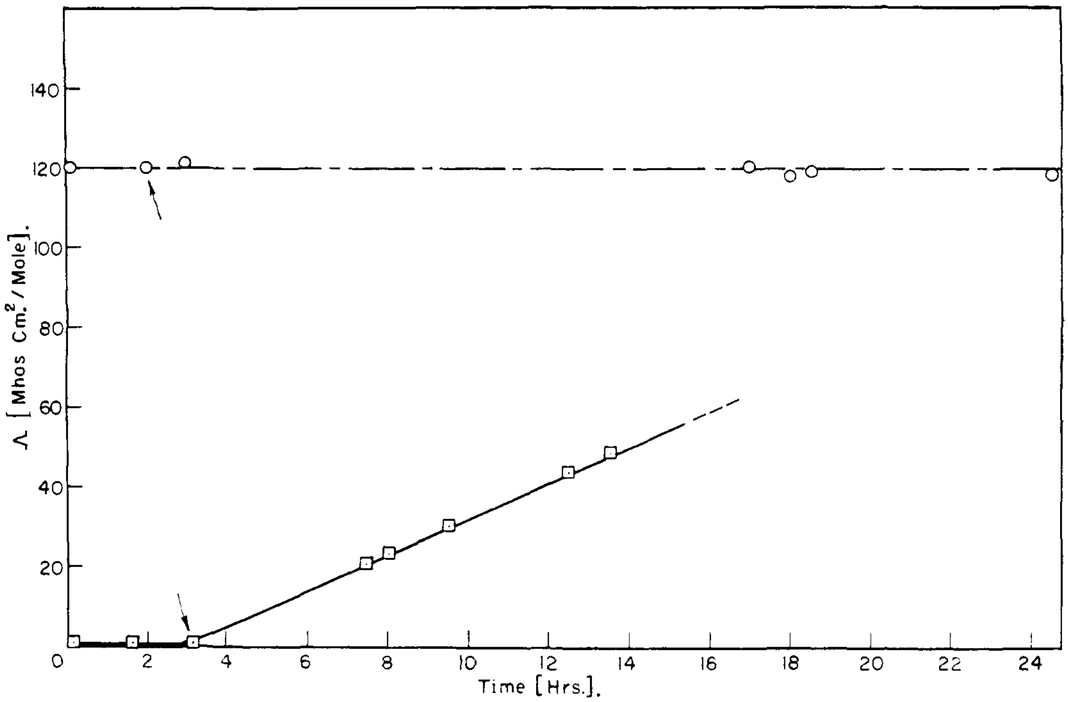

Fig. 2.—The effect of near ultraviolet light on the conductivity of hexaphenylethane solutions at 0°; arrow indicates the time at which illumination was started: —□—, degassed SO_2, 6750 liters/mole; —O—, oxygenated SO_2, 2600 liters/mole.

compared in Fig. 3 with the straight line Shedlovsky plot obtained from the data for a typical 1:1 electrolyte. There is, however, the possibility that the sulfur dioxide solution of the oxygenation product contains several electrolytes, and that the similarity to 2:1 electrolyte behavior is illusory. No evidence on the nature of the anion was obtained other than the failure to detect sulfate in the hydrolyzate.

TABLE III

CONDUCTIVITY OF TETRAMETHYLAMMONIUM SULFATE AND OXYGENATED HEXAPHENYLETHANE IN SULFUR DIOXIDE

$[(CH_3)_4N]_2SO_4$[a]			Ph_6C_2[b]		
v, l./mole	$\kappa \times 10^6$, mhos[c] cm.$^{-1}$	Λ, mhos-cm.^{2} mole^{-1}	v, l./mole	$\kappa \times 10^6$, mhos[c] cm.$^{-1}$	Λ, mhos-cm.^{2} mole^{-1}
170.0	292.4	49.71	218	133.3	29.1
387.2	164.2	63.58	499	66.0	32.9
882.7	90.69	80.05	1140	31.8	36.3
2013	49.21	99.06	2610	15.1	39.2
4590	25.72	118.0	5960	6.99	41.7
10470	13.02	136.3	13600	3.27	44.6
23870	6.547	156.3	31200	1.61	50.4
54450	3.511	191.2	71500	0.89	64.2
124100	2.102	260.8	164000	0.58	89.8

[a] 0.12 ± 0.03°. [b] Partially oxygenated solution, light excluded, −8.93°. [c] Corrected for solvent conductivity.

Discussion

It is now apparent that earlier work involved solutions in sulfur dioxide of hexaarylethanes that were either completely oxygenated or nearly so. Although spectroscopic and magnetic studies on oxygen-free solutions in sulfur dioxide are lacking, qualitative observations of color, oxygen absorption and sensitivity to irradiation as well as conductivity data make it seem highly probable that the usual triphenylmethyl–hexaphenylethane equilibrium mixture is present in such solutions.

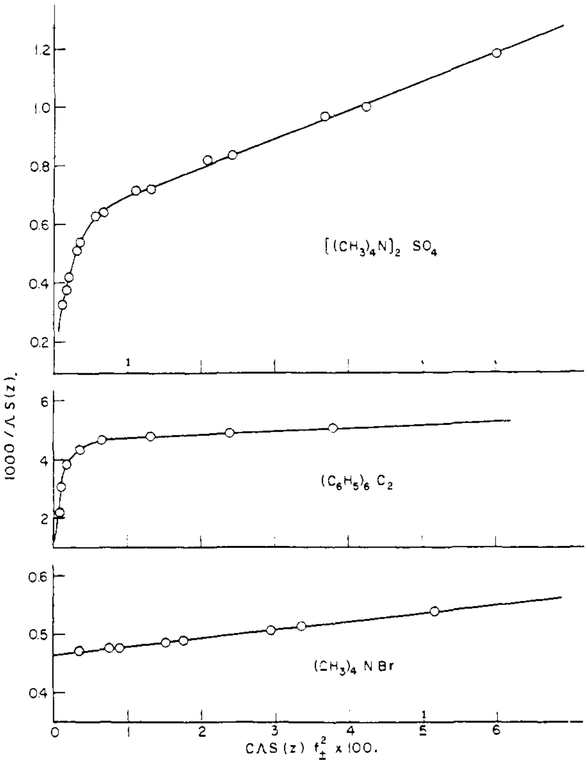

Fig. 3.—Shedlovsky plots for salts in sulfur dioxide solution.

The unusual character of these solutions relates to the formation of electrolytes on reaction with oxygen or with light. An attractive interpretation of the oxygenation reaction assumes that this represents an extreme case of attack on the solvent. Much less extensive attack on other solvents, presumably involving triphenylmethylperoxy radical[26] is well established. The present data suggest that a triphenylcarbonium salt of a dinegative anion is formed. In the absence of knowledge concerning the nature of the anion or even the stoichiometry of oxygen consumption,[27] the system cannot be more completely defined.

The product of irradiation in the absence of oxygen apparently is different from that obtained in other media where triphenylmethane and diphenyl-bis-diphenyleneethane result from induced disproportionation. A reasonable hypothesis is that generation of conducting species in the present case involves attack on the solvent but diagnostic data are not now available.

Acknowledgment.—This work was made possible by a Frederick Gardner Cottrell grant by the Research Corporation. Mr. Peter Pappas assisted in some of the experiments. Valuable discussions were held with Dr. George R. Thomas.

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[26] *Cf.* N. N. Lichtin and G. R. Thomas, THIS JOURNAL, **76**, 3021 (1954).

[27] A single rough quantitative oxygenation experiment indicated consumption of 0.7 mole of O_2 per mole of hexaphenylethane. Additional experiments by P. Pappas yielded results of poor precision which fell in the range 1 ± 0.5 mole of O_2 per mole of hexaphenylethane.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Reaction of Nitric Oxide with Isobutylene

BY JOHN F. BROWN, JR.

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Nitric oxide containing traces of nitrogen dioxide reacts readily with liquid isobutylene to give nitrogen and a mixture of nitrated products. This mixture is believed to contain β-nitroisobutylene (22%); nitro-*t*-butanol (9%); traces of isobutylene pseudonitrosite, nitro-*t*-butyl nitrate and α-hydroxyisobutyraldoxime; and major amounts (66%) of a substance having the partial structure (nitro-*t*-butyl)$_4N_2O_2$. The latter is very unstable and decomposes on standing or gentle warming to give α-nitroisobutylene and N-(nitro-*t*-butyl)-hydroxylamine, which also decomposes on standing or heating. Thus, the net result of treating isobutylene with nitric oxide and then distilling the product is the formation of nitroisobutylenes (74%) and small quantities of substances having nitro-*t*-butyl groups joined to nitro, nitroso, nitrate ester, hydroxyl, hydroxylamino and oximino groups. It is suggested that the (nitro-*t*-butyl)$_4N_2O_2$ is representative of the unidentified unstable oils which have frequently been obtained by treating olefins with N_2O_3 or N_2O_4. A mechanism for the NO–isobutylene reaction is proposed.

In the past, the nature of the reaction between nitric oxide and olefins has been virtually unknown. There are about a dozen references in the technical literature suggesting the possibility of such a reaction, but the only workers to identify any products were Bloomfield and Jeffrey,[1] who obtained 1-nitrocyclohexene and cyclohexene pseudonitrosite from cyclohexene. As late as 1949, an authoritative text stated that reactions between nitric oxide and the normal ethylenic double bond did not occur.[2]

An extensive study of the nitric oxide–olefin reaction has recently been made in this Laboratory. This study established three general characteristics of the reaction. First, the reaction is initiated by nitrogen dioxide. Scrupulously purified nitric oxide can be stored in contact with liquid olefins for days without reaction, but in the presence of traces of NO_2, such as are usually present in nitric oxide, reaction occurs readily with many types of olefins and other hydrocarbons.[3] Second, the product of a nitric oxide–olefin reaction is usually a mixture of the crystalline pseudonitrosite (dimeric nitro nitroso adduct) and an unstable liquid mixture which will undergo a "fume-off" or low-order explosion upon attempted distillation. It was found that the decomposition of these liquids could be controlled by steam distillation or passage through a falling film still, but no means of fractionating any significant quantity without decomposition was discovered. Third, the distilled liquid reaction products consist mainly of mixtures of nitroölefins. For example, 1-octene gives 1-nitro-1-octene and 1-nitro-2-octene.[3] In general, the linear olefins give fair yields of both nitroölefins and pseudonitrosites, while the branched olefins give good total yields of nitroölefins but little pseudonitrosite.

It was evident, however, that any detailed understanding of the nitric oxide–olefin reaction would require considerably more information about the nature of the reaction products. The present investigation of the products from the nitric oxide–isobutylene reaction was undertaken in order to obtain such information.

Basically, this objective required that a detailed analysis be made on a complex mixture which was changing composition continually during the course of the analysis. In order to accomplish this, a large batch of nitric oxide–isobutylene reaction product was prepared and the stoichiometry of the reaction determined. The product was fractionated, mainly by distillations under mild conditions, until a large number of fractions representing individual compounds or simple mixtures had been obtained. Analysis of these then permitted a

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[1] G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944).

[2] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," The Clarendon Press, Oxford, 1949, p. 213.

[3] C. A. Burkhard, J. F. Brown, Jr., C. S. Herrick, R. L. Myers and D. T. Hurd, Abstracts of Papers, 126th Meeting American Chemical Society, September 12–17, 1954, p. 42-O.