silver–silver bromide electrode is found to be 0.07111.

The author extends his thanks to Professor Herbert S. Harned for advice and suggestions during the course of this work.

Summary

1. A type of silver–silver bromide electrode prepared in a novel manner has been described.

2. Measurements of the cell

$$H_2 \text{ (1 atm.)} \mid HBr(m) \mid AgBr \mid Ag$$

have been made at concentrations from 0.0001 to 0.02 M in quartz and Pyrex glass cells of very simple design.

3. Agreement with the limiting law of Debye and Hückel has been obtained.

4. The value of the molal electrode potential of the silver–silver bromide electrode has been found to be 0.0711 volt.

NEW HAVEN, CONN. RECEIVED JUNE 28, 1935

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Absorption Spectra of Free Radicals

BY LEIGH C. ANDERSON

The cause of the color of solutions of free radicals has been the subject of considerable discussion.[1] Most investigators agree that the color is associated with the free radical, for example, triphenylmethyl, rather than the dimolecular form, hexaphenylethane. For a number of years after the discovery of free radicals, many writers thought that the presence of trivalent carbon in the triarylmethyl radicals produced by dissociation of the hexaphenylethane was sufficient reason alone for the color of such solutions. However, after Gomberg[2] demonstrated the reactivity of para substituted halogens in triarylmethyl halides, the question of quinonoidation of the free radicals was given more consideration. In 1923, Gomberg and Blicke[3] published some studies on the chemical reactions of para halogenated triarylmethyls and presented data which also indicated in a conclusive manner the existence of a quinonoid modification of the free radical. Visual comparison of the color of the solutions, as well as qualitative absorption spectra, have indicated the similarity of light absorption of sulfur dioxide solutions of a triarylmethyl radical to the light absorption of corresponding solutions of the triarylmethyl halides and sulfate.[4] The qualitative absorption spectrum of the negative triphenylmethyl ion was reported by Hein[5] and the spectrum was shown to be quite different from that of the corresponding free radical or that of the cation. In this paper we are presenting conclusions based on data obtained from quantitative absorption spectra of free radical solutions.

Previous investigators[6] have shown that the triphenylmethyl halides are electrolytes when dissolved in sulfur dioxide. The quantitative absorption spectrum curve for a solution of triphenylbromomethane (Curve 2, Fig. 1) in sulfur dioxide is, therefore, the curve for the triphenylmethyl cation. It is very similar to the curve for the triphenylmethyl cation in solution in sulfuric acid, perchloric acid or dimethyl sulfate.[7] In sulfur dioxide the frequencies of maximum absorption for the triphenylmethyl cation are shifted toward the longer wave lengths but otherwise the shape and height of the curves are almost identical with those in the above-named solvents. In the publication just referrred to, we presented evidence, based on quantitative absorption spectra data, that the triphenylmethyl cation exists in a quinonoid modification in solvents like sulfuric acid, and the present data indicate that this cation exists in a quinonoid modification in sulfur dioxide as well.

The curve for a solution of the free radical, triphenylmethyl, in ether (Curve 1) has a group of narrow bands in the visible region near the ultraviolet. When this curve is compared with the

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(1) A more complete discussion of the early work on this subject than is included in this paper is presented in Schmidlin, "Das Triphenylmethyl," Verlag von F. Enke, Stuttgart, 1914; and Walden, "Chemie der freien Radikale," Verlag von S. Hirzel, Leipzig, 1924.

(2) Gomberg, *Ber.*, **40**, 1851 (1907).

(3) Gomberg and Blicke, THIS JOURNAL, **45**, 1765 (1923).

(4) Meyer and Wieland, *Ber.*, **44**, 2557 (1911); Schmidlin and Garcia-Banûs, *ibid.*, **45**, 3187 (1912); Tschitschibabin, *J. prakt. Chem.*, **88**, 511 (1913).

(5) See Hantzsch, *Ber.*, **54**, 2619 (1921).

(6) Walden, *ibid.*, **35**, 2018 (1902); Gomberg, *ibid.*, **35**, 2403 (1902).

(7) Anderson, THIS JOURNAL, **52**, 4567 (1930).

absorption curves for ether solutions of benzoquinone, quinone-monoxime, quinone-monochlorimine, etc.,[8] one finds the same type of absorption and we believe this is evidence that the non-ionized free radical exists in a quinonoid modification. In the case of triphenylmethyl, the height of these bands, as will be discussed later in this and in subsequent papers, is very dependent upon the temperature which, with a given free radical solution, is the determining factor on the extent of dissociation.[9] These bands, therefore, furnish not only a definite clew to the presence of the non-ionized free radical, but also a means of determining the quantity present. Ziegler and Ewald,[10] from quantitative absorption spectra data obtained from measurements of the height of these bands, calculated the heat of dissociation of free radicals.

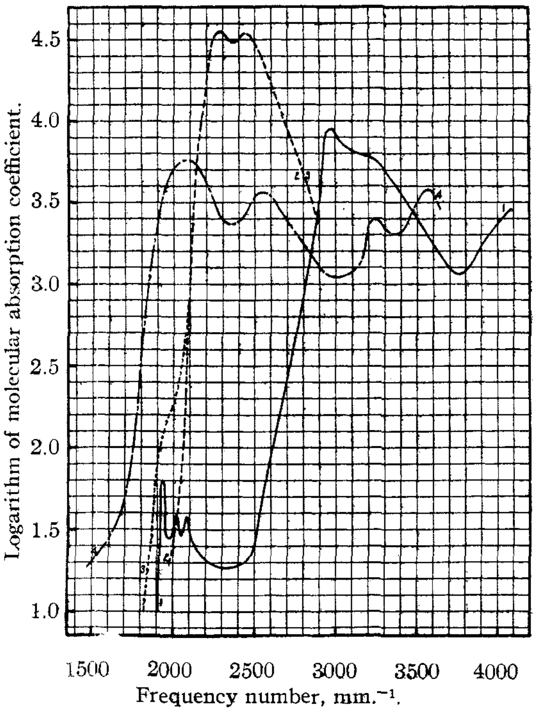

Fig. 1.—1, Triphenylmethyl in ether; 2, triphenylbromomethane in sulfur dioxide; 3, triphenylmethyl in sulfur dioxide; 4, sodium triphenylmethyl in ether.

Walden[11] measured the conductivity of sulfur dioxide solutions of triphenylmethyl and showed that the free radicals are electrolytes in this solvent. Leaving out of consideration possible solvation of the ions, ionization of triphenylmethyl in solution in sulfur dioxide can be postulated as follows

$$(C_6H_5)_3C = [(C_6H_5)_3C]^+ + \ominus \qquad (1)$$

$$(C_6H_5)_3C + \ominus = [(C_6H_5)_3C]^- \qquad (2)$$

Gomberg,[12] Hantzsch[13] and Cole[14] have expressed the opinion that sulfur dioxide solutions of triphenylmethyl may perhaps contain both the cation and anion of triphenylmethyl. The curve that we obtained for sulfur dioxide solutions of triphenylmethyl (Curve 3) is so similar to that for corresponding solutions of triphenylbromomethane that one is led to the conclusion, immediately, that the quinonoid triphenylmethyl cation is present. Furthermore, in dilute solutions, the height of the quantitative absorption curve shows that, within experimental error, the same amount of triphenylmethyl cation is produced in the free radical solution as is produced from an equivalent solution of triphenylbromomethane. Because the absorption for a dilute solution of the bromide (top part of curve) is practically unchanged by a change in temperature, we believe that the salt is completely ionized. If that conclusion is correct, it is apparent that in dilute sulfur dioxide solutions of hexaphenylethane, there is not only complete dissociation of the ethane into the free radical but at the same time quantitative formation of the triphenylmethyl cation. Obviously, the curve for the cation in this case should be measurably lower if any appreciable amount of the triphenylmethyl were present as triphenylmethyl anion. We conclude, therefore, that the reaction indicated by equation (2) occurs to a very small extent, if at all, and that the solution consists of triphenylmethyl in equilibrium with the triphenylmethyl cation and an electron, with solvation, of course, by the sulfur dioxide. The long wave length edge of the absorption band in the more concentrated solutions of triphenylmethyl in sulfur dioxide (lower part of curve) extends further into the visible region than does the curve for corresponding solutions of triphenylbromomethane. When the curve for triphenylmethyl in sulfur dioxide is compared with the curves for ether solutions of triphenylmethyl and for the sodium triphenylmethyl compound (Curve 4), one may infer that the presence of either non-ionized triphenylmethyl or of some of

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[8] Anderson and Geiger, THIS JOURNAL, **54**, 3067 (1932); Anderson, *ibid.*, **55**, 2095 (1933).

[9] Piccard, *Ann.*, **381**, 347 (1911).

[10] Ziegler and Ewald, *ibid.*, **473**, 163 (1929).

[11] Walden, *Z. physik. Chem.*, **43**, 385 (1903); see also Gomberg, *Ber.*, **36**, 3929 (1903); Gomberg and Cone, *ibid.*, **37**, 2045 (1904).

[12] Gomberg, *ibid.*, **35**, 2406 (1902).

[13] Hantzsch, *ibid.*, **54**, 2607 (1921).

[14] Cole, *Philippine J. of Sci.*, **19**, 681 (1921).

the triphenylmethyl anion might account for this displacement. On the basis of our conclusion in the case of the dilute solutions, we conclude that the greater absorption observed in the visible region in the case of the more concentrated solutions is due to the non-ionized triphenylmethyl radical rather than the anion.

The absorption of triphenylmethyl in ether is very sensitive to temperature changes. For example, the narrow band at about 1935 mm.$^{-1}$ has a maximum value (expressed as logarithm of the molecular absorption coefficient) of 1.83 at 23°, 1.38 at 0° and 1.10 at $-20°$. Solutions of the free radical in sulfur dioxide show, on the contrary, the opposite effect in the more concentrated solutions, and in the dilute solutions they are almost identical at room temperature and at $-50°$. The sodium triphenylmethyl solution for which the curve is presented shows only a slight thermal effect which is similar to that noted with the sulfur dioxide solutions of triphenylmethyl. If the intensity of absorption by the ionized free radical is proportional to the degree of dissociation of the hexaphenylethane and subsequent ion-formation from the triphenylmethyl, these solutions behave like solutions of strong electrolytes with ionization increasing as the temperature is lowered. This temperature effect on the absorption is in the same direction as the temperature effect observed by Gomberg and Sullivan[15] on the ionization of triphenylbromomethane in sulfur dioxide. Walden[16] ascribes this effect to a decrease in solvation at higher temperatures. Although conductivity data indicate that triphenylbromomethane is ionized to a much greater extent than is triphenylmethyl, it is of interest to point out again that the height of the quantitative absorption curve for the triphenylmethyl cation is identical, within experimental error, for very dilute solutions of these two compounds. The solution of sodium triphenylmethyl for which data are here being presented was very dilute and the change in absorption was small even when the temperature was lowered from 25 to $-67°$.

Experimental

The solutions of triphenylmethyl were prepared in a unit consisting of the parts lettered A to L in Fig. 2. About 0.5 g. of pure molecular silver was placed in a tube (A) sealed to the bottom of a small calibrated flask (B), and to the neck of the latter were sealed several absorption cells (C) and an inlet (D) and an outlet tube (E). The weighed sample of pure triphenylbromomethane in a micro beaker (F) was lowered into the neck and rested on the top of the insealed inlet tube. The top of the flask was then sealed off (G). Nitrogen which had been purified by passage through three towers of alkaline sodium hydrosulfite, an alkaline cuprous carbonate-copper absorption system as recommended by Van Brunt,[17] several sulfuric acid washes, an ascarite tower, two calcium chloride towers and finally one magnesium perchlorate tower, was passed through a distilling flask (H) and then through the absorption unit and out through a mercury trap (J). After passing nitrogen through for several hours, the silver was heated to 150° for half an hour by a small electric heater. Pure absolute ether was introduced into the distilling flask (H) in such a manner that no air could enter the apparatus, and the requisite amount of ether was then distilled into the bulb containing the silver.

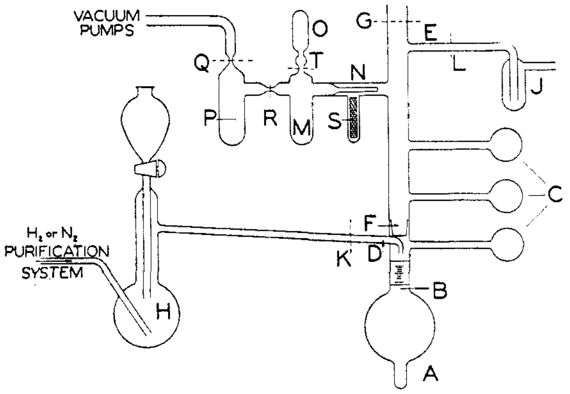

Fig. 2.

The flow of nitrogen was continued while the ether in the bulb was frozen by liquid air, and the bulb, together with the absorption cells, was sealed off (at K and L) from the rest of the line. After the ether had warmed to room temperature, the bulb was tilted and the triphenylbromomethane dissolved. The mixture was shaken, taking care that no silver or silver halide entered the absorption cells. When reaction was complete, the precipitate of silver and silver bromide was allowed to settle and the clear supernatant solution of triphenylmethyl was decanted into the absorption cells.

The solution of sodium triphenylmethyl was prepared in the same type of apparatus. Sodium amalgam was prepared in a tube (M), which was separated from the main unit by a breakable inseal (N), as follows. The tube and auxiliary traps, one containing sodium (O) and the other mercury (P), were evacuated and the sodium was melted and separated from surface oxide by filtration through two capillaries (T), after which the capillary nearest the filtered sodium (in M) was sealed off. The mercury trap (P) and tube (M) were then sealed off (at Q) from the pumps, and after distilling the mercury into the sodium, the mercury trap was sealed off (R). Pure hydrogen was passed through the ether (H), which was kept over sodium-potassium alloy, and through the unit (A-L) for a

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(15) Gomberg and Sullivan, THIS JOURNAL, **44**, 1818 (1922).

(16) Walden, "Chemie der freien Radikale," p. 145.

(17) Van Brunt, THIS JOURNAL, **36**, 1448 (1914).

number of hours and the requisite amount of ether was then distilled into B. After freezing the ether in liquid air, the unit was evacuated and sealed at K and L. On inverting the apparatus the bromide was dissolved and an iron weight, sealed in glass (S), broke the inseal (N). The solution on coming in contact with the sodium amalgam first acquired the yellow color of the free radical and finally the reddish-orange color of the sodium derivative. The curve for the absorption spectrum of sodium triphenylmethyl, which is presented in this paper, was obtained for a 0.0011 molar solution of triphenylmethyl in contact with a 10% sodium amalgam containing 0.025 mole of sodium. The curve that was obtained shortly after the color of the sodium derivative appeared in the solution showed the presence not only of the metal derivative, but also of the free radical (detected by the band at about 3000 mm.$^{-1}$). The curve as presented was obtained after the system had been shaken until it reached equilibrium.

Sulfur dioxide solutions of triphenylmethyl were prepared in two ways: first, by the reaction in that solvent of a known amount of triphenylbromomethane and silver; and, second, by the use of a known amount of crystalline triphenylmethyl, previously prepared. The identical absorption curve was obtained by either method.

Other investigators have reported that triphenylmethyl in sulfur dioxide does not react with oxygen. This observation has been corroborated. When the sulfur dioxide was evaporated and pure ether added, the absorption spectrum, typical of the ether solution, was obtained and from this ether solution the peroxide was obtained. The yellow residue obtained upon evaporation of the sulfur dioxide was only partially soluble in ether and even after boiling the mixture the residue retained the odor of sulfur dioxide, showing that a complex of free radical and sulfur dioxide was formed that is quite stable at ordinary temperatures.[18]

The temperature of the air-bath which was used for the low temperature spectral work was ascertained with a calibrated copper–constantan thermocouple and potentiometer. The apparatus and procedure for obtaining the quantitative absorption spectra has been described.[19]

Summary

1. Curves are presented for the quantitative absorption spectrum of each: ether solutions of triphenylmethyl and of the sodium derivative of triphenylmethyl, and sulfur dioxide solutions of triphenylbromomethane and of triphenylmethyl.
2. The data indicate that triphenylmethyl exists in a quinonoid modification in solution in ether and in sulfur dioxide.
3. When dissolved in sulfur dioxide, triphenylmethyl is in equilibrium with the triphenylmethyl cation and an electron, with solvation, of course, of the ions.

ANN ARBOR, MICHIGAN RECEIVED JULY 2, 1935

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[18] Schlenk and Weickel have described an addition compound from tribiphenylmethyl and sulfur dioxide [*Ann.*, **372**, 11 (1909)].

[19] Anderson and Gomberg, This Journal, **50**, 203 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RHODE ISLAND STATE COLLEGE]

The Hexammine Cobaltic Compounds in the Gravimetric Determination of Vanadium[1]

BY W. GEORGE PARKS AND H. J. PREBLUDA

M. Parks[2] in the development of a gravimetric method for the determination of vanadium, found that the addition of hexammine cobaltic ion to a neutral solution of the metavanadate results in an apricot colored precipitate which when ignited gives a mixture of oxides represented by $2CoO\cdot 3V_2O_5$. Addition of the $Co(NH_3)_6^{+++}$ ion to an alkaline solution results in the precipitation of an orange colored precipitate which on ignition yields a mixture of oxides represented by $4CoO\cdot 3V_2O_5$. The metavanadate ion in a solution acidified with acetic acid and ammonium acetate (*p*H 5.1) gives a yellow precipitate which on ignition yields a mixture of oxides represented by $2CoO\cdot 9V_2O_5$. In this acid medium the metavanadate may be separated quantitatively from phosphate, arsenate, ferric, cupric and calcium ions. It cannot be separated from tungstate, molybdate or lead ions.

Parks assumed that hexammine cobaltimetavanadate $Co(NH_3)_6(VO_3)_3$ was formed in a neutral solution, hexammine cobaltipyrovanadate $[Co(NH_3)_6]_4(V_2O_7)_3$ in a basic solution and hexammine cobaltideuterohexavanadate $[Co(NH_3)_6]_4(V_6O_{17})_3$ in an acid solution because these formulas were the only possibilities consistent with the data obtained from the ignited oxides.

This investigation was undertaken to establish the definite composition of these compounds by chemical analysis.

Preparation of Materials

Ammonium Metavanadate Solution.—A sample of c. p. NH_4VO_3, furnished by the Vanadium Corporation of America, was recrystallized three times from distilled

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[1] This paper is from a thesis submitted by H. J. Prebluda to the Faculty of Rhode Island State College in partial fulfilment of the requirements for the degree of Master of Science.

[2] M. Parks, "Dissertation," Columbia University, 1930.