Pearl Polymerization of 3-Trifluoromethylstyrene.—The procedure was analogous to that described by Hohenstein, Vingiello and Mark[20] for styrene. Adjustment of the specific gravity of the aqueous phase with salt was necessary because of the high density of the fluorinated styrene. A mixture of 25 g. of 3-trifluoromethylstyrene, 0.25 g. of benzoyl peroxide, 500 g. of water, 76.5 g. of sodium chloride and 2.6 g. of talc was agitated slowly by means of a propeller-type stirrer at 80–85° for five hours. The resulting pearls were hard and translucent with an average diameter of 1–2 mm.; molecular weight 9370 (viscosity method, $K = 0.45 \times 10^4$, Kemp and Peters[21]).

Emulsion Polymerization of 3-Trifluoromethylstyrene.—Mixtures of 75 g. of 3-trifluoromethylstyrene, 450 ml. of water, 5 ml. of Tergitol Penetrant No. 4 and 0.15 g. (0.2%) of $K_2S_2O_8$ in each of 3 quart bottles were rotated in a polymerization bath at 40° for six days. The polymer was then coagulated by a saturated salt solution, washed, and dried. A molecular weight determination gave a value of 74,000 (Kemp and Peters[21] equation).

The solubility characteristics of this polymer were determined and compared with those of polystyrene (mol. wt. 47,700). Under comparable conditions, polytrifluoromethylstyrene and polystyrene were soluble in chloroform, trichloroethylene, toluene, benzotrifluoride and dioxane. Benzene and carbon tetrachloride swelled the fluorinated polymer and dissolved polystyrene. Acetone, ethyl alcohol and ether dissolved the fluorinated polystyrene while polystyrene was insoluble. Petroleum ether swelled the fluorinated styrene and did not dissolve polystyrene, while nitroethane dissolved the polyfluorostyrene but only swelled the polystyrene.

Copolymerizations.—Copolymers of the fluorinated styrenes with vinyl acetate, methyl methacrylate, styrene and maleic anhydride were prepared by heating the mixed monomers at 70° in the presence of benzoyl peroxide. Typical, hard, transparent or translucent polymers resembling polystyrene were obtained in all cases except those involving α- or β-methylstyrenes with vinyl acetate, which failed to copolymerize. Elastic copolymers with butadiene were prepared using the usual GR-S synthetic rubber emulsion system with styrene replaced by the fluorinated styrenes. Only the β-methylstyrene failed to copolymerize. The properties of these copolymers will be described elsewhere.

Summary

1. The preparation of seven fluorinated styrenes, five of which are new, is described.

2. A study has been made of the polymerization and copolymerization characteristics of these styrenes.

LAFAYETTE, INDIANA RECEIVED FEBRUARY 8, 1947

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(20) Hohenstein, Vingiello and Mark, *India Rubber World*, **110**, 291–294 (1944).

(21) Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

A Precise Method for the Determination of the Ionization Constants of Some Weak Organic Acids[1]

BY RICHARD S. STEARNS[2] AND GEORGE W. WHELAND

Introduction

The present investigation has as its purpose the determination, by a spectrophotometric method, of the ionization constants of 4,4′,4″-trinitrotriphenylmethane, 2,4-dinitrodiphenylamine, 2,4-dinitroaniline, and 4-nitrodiphenylamine in ethanol, and of *p*-nitrobenzyl cyanide in water.

Theory of the Method

The method chosen for the determination of the ionization constants of the weak acids investigated here depends upon the fact that there is a difference between the positions of the absorption maxima of the undissociated compound, HR, and ion, R^-. This shift in the absorption maximum is illustrated in Fig. 1, where the curves for the absorption of light by 2,4-dinitroaniline in neutral and alkaline ethanol are plotted. This pronounced shift in the absorption maximum on ionization allows the concentration of the negative ion to be determined by standard spectrophotometric methods, provided Beer's law is obeyed and provided that the extinction coefficient of the colored ion is known.

The compounds investigated here are so weakly acidic that it is impossible to force the equilibrium of the reaction

$$\mathrm{HR} + \mathrm{OEt}^- \rightleftarrows \mathrm{R}^- + \mathrm{HOEt} \qquad (1)$$

so far to the right that virtually all of the compound HR is in the form of the ion R^-. Consequently, the extinction coefficient of the ion can not be calculated directly from the relation

$$kd = \log \frac{I_0}{I} \Big/ [\mathrm{R}^-] \qquad (2)$$

where k is equal to the molar extinction coefficient, $[\mathrm{R}^-]$ is the concentration of R^- in moles per liter, d is the length of light path in centimeters, and I_0/I is the reciprocal of the fraction of light transmitted. Here, and throughout the remainder of this paper, the extinction coefficient of the ion R^- is assumed to be much greater, at the wave length used, than that of the un-ionized acid HR. In order to overcome the difficulty just referred to, a formula was developed which expresses an apparent extinction coefficient as a function of the concentration of base, and allows the true extinction coefficient at a given wave length to be determined by a short extrapolation.

If the concentration of the solvent ethanol is assumed constant, the equilibrium expression for the reaction written in equation 1 above is

$$K_e = (\mathrm{R}^-)/(\mathrm{HR})(\mathrm{OEt}^-) \qquad (3)$$

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(1) This paper comprises a part of the subject matter of a thesis submitted by Richard S. Stearns in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago.

(2) Present address: Chemical and Physical Research Laboratories, Firestone Tire and Rubber Company, Akron, Ohio.

where the quantities in parentheses represent activities. Since the activity of any substance is equal to its concentration multiplied by its activity coefficient γ, equation 3 may be written

$$K_e = \frac{\gamma_{R^-}[R^-]}{\gamma_{HR}[HR]\,\gamma_{OEt^-}[OEt^-]} \qquad (4)$$

It is usually assumed that γ_{HR} is equal to unity, and this assumption is probably true in the concentrations used here, which are of the order of 10^{-4} mole/liter. If the Debye–Hückel limiting law holds in ethanol solutions, then the activity coefficients of ions of the same charge type in solutions of equal ionic strength are equal and therefore γ_{R^-} and γ_{OEt^-} in equation 4 cancel, and we have for the thermodynamic equilibrium constant of reaction 1

$$K_e = [R^-]/[HR][OEt^-] \qquad (5)$$

Since the ratio of $[R^-]$ to $[HR]$ is therefore constant for any specified value of $[OEt^-]$, the apparent extinction coefficient k', which is defined by the equation

$$k'd = \log\frac{I_0}{I}\Big/\{[R^-] + [HR]\} \qquad (6)$$

is seen to be independent of the value of $[R^-] + [HR]$ if Beer's law is obeyed, even though it should be dependent on that of $[OEt^-]$.

Comparison of equations 2 and 6 shows that

$$[RH] = [R^-]\left(\frac{k}{k'} - 1\right) \qquad (7)$$

Insertion of equation 7 in equation 5 and rearrangement of terms leads to the final equation

$$\frac{1}{k'} = \frac{1}{k} + \frac{1}{[OEt^-]}\left(\frac{1}{kK_e}\right) \qquad (8)$$

This equation gives $1/k'$ as a linear function of $1/[OEt^-]$. Now, $1/k'$ can be determined experimentally from equation 6. Moreover, the equilibrium concentration of ethoxide ion is known to a very good approximation, because the amount of the compound HR used is so small compared to that of the sodium ethoxide that, even if all of it were converted to the ion, the concentration of ethoxide ion would not be changed appreciably. Thus, as a typical example, in one experiment with 4,4′,4″-trinitrotriphenylmethane the original concentration of the methane HR was equal to 2.655×10^{-5} mole per liter and the original concentration of OEt^- was 1.254×10^{-2} mole per liter. Even if at equilibrium all the HR were converted to R^-, the concentration of OEt^- would still be 1.251×10^{-2}. The uncertainty regarding the equilibrium concentration of ethoxide ion therefore introduces a maximum error of less than 0.3%. It is, accordingly, possible to consider that the symbol $[OEt^-]$ in equation 8 means the original concentration of ethoxide ion before the addition of the weak acid HR. If, now, the values of $\log I_0/I$ are measured at a given wave length in solutions of different base strength, and if the resulting values of $1/k'$ are plotted against $1/[OEt^-]$, a straight line is obtained, the intercept of which is equal to the reciprocal of the true extinction coefficient k at the given wave length. From the slope of the line, knowing k, we can calculate K_e. Provided that the approximations we have made are valid, K_e is the thermodynamic equilibrium constant.

The solvolysis constant K_h is equal to $1/K_e$ and the dissociation constant for the reaction

$$RH \rightleftarrows R^- + H^+$$

is

$$K_a = \frac{(R^-)(H^+)}{(RH)} = \frac{K_s}{K_h}$$

where K_s is the ion product of the solvent. The ion product of ethanol has been determined by Danner[3] to be 7.28×10^{-20} at 25°.

Experimental

The measurements made in this research required a spectrophotometer that would give a narrow band-width and also would give accurate values of I_0/I, the fraction of light transmitted. The instrument chosen was essentially the one used by Klotz.[4] Values of I_0/I with a maximum error of ± 0.005 were obtained; for values of I_0/I between 3.000 and 7.000 an error of about 0.1% is thus introduced. The measured band width at half maximum intensity and at a wave length of 5500 Å. was 25 Å. A temperature of $25 \pm 0.2°$ was maintained in the thermostat.

For those compounds where the shift of the maximum of the absorption band on ionization is not very large, *i. e.*, where the undissociated compound as well as the ion is colored, it was necessary to make the optical measurements on the side of the absorption band of the ion in order to avoid absorption of light by the undissociated compound. The absorption curve of the acid HR usually has a long tail not shown in Fig. 1, which has appreciable magnitude at the maximum absorption for the ion. For measurements of this type, where there is a large change in the extinction coefficient over a small wave length band, Beer's law is not obeyed unless the band width used in the measurements is very small. In order to be sure that we were using band widths which were sufficiently narrow, the optical density of solutions of potassium permanganate were measured at the absorption maximum and at the side of a steep band[5] where the change of the extinction coefficient per ångström was of the same order as that of the colored negative ions at the wave length used for the absorption measurements. It was found that Beer's law was well obeyed over a concentration range of twenty, where the optical density, $\log I_0/I$, varied from 0.00 to 1.10, both at the peak and at the side of the band. Further evidence that the band widths employed were sufficiently narrow will be described below.

The solutions used were made up in absolute ethanol. Commercial absolute alcohol was found by density measurements to be 99.5% ethanol, the impurity being assumed to be water. The alcohol was dried by refluxing over magnesium ethoxide and distilling. The alcohol had been dried commercially by the distillation of a benzene mixture, and the dry ethanol was found by spectrophotometric methods to contain 0.006% benzene. That this small amount of benzene did not affect our measurements was shown in several experiments in which benzene-free ethanol was used.

The sodium ethoxide was prepared by refluxing the absolute ethanol in a stream of dry nitrogen to remove carbon dioxide and oxygen and then adding sodium which had been cleaned and rinsed in absolute alcohol. The sodium ethoxide was standardized against standard potassium acid

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[3] P. S. Danner, THIS JOURNAL, **44**, 2832 (1922).

[4] I. M. Klotz, Ph.D. Dissertation, University of Chicago, 1940, and *Ind. Eng. Chem., Anal. Ed.*, **15**, 277 (1943).

[5] A. Hagenbach and R. Percy, *Helv. Chim. Acta*, **5**, 454 (1922).

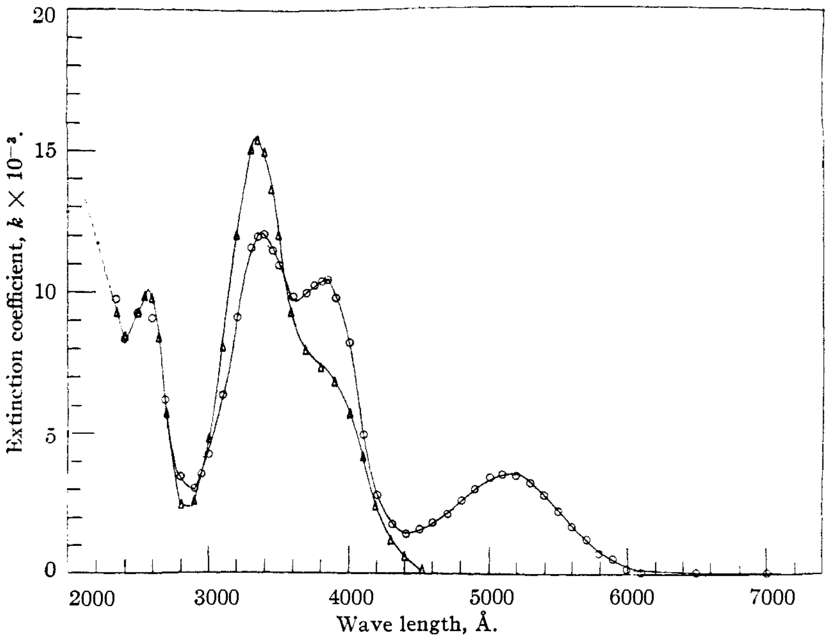

Fig. 1.—Shift in absorption spectrum of 2,4-dinitroaniline on addition of base: Δ, 2,4-dinitroaniline in ethanol; O, 2,4-dinitroaniline in 0.1 N sodium ethylate.

phthalate by titration, with phenolphthalein as the indicator.

The compounds used in this investigation were either available commercially or had been previously prepared by students in this laboratory. All compounds were recrystallized until melting points checked the values given in the literature and until the apparent extinction coefficient at a given concentration of base did not change on further recrystallization.

The procedure followed in the determination of the ionization constants of 2,4-dinitrodiphenylamine, 2,4-dinitroaniline, and 4-nitrodiphenylamine will be described first. Stock solutions of the compounds in absolute ethanol were prepared. The solutions, the optical density of which were to be measured, were prepared by weighing 0.5 g. or more of the stock solution of the compound into a 25.00-cc. or a 50.00-cc. volumetric flask, adding a known volume of standardized sodium ethoxide by means of a pipet or a buret and diluting to volume with absolute ethanol.

For these substances it was necessary to make the absorption measurements on the side of an absorption band in order to avoid the absorption by the undissociated compound.[6] It was found that the greatest precision could be obtained by making a series of measurements in a given concentration of sodium ethoxide with increasing concentrations of the compound under investigation.

Reference to equation 6 shows that, if Beer's law is obeyed, a straight line with slope equal to $k'd$ and with intercept at the origin should be obtained when $\log I_0/I$ is plotted against $[R^-] + [HR]$ for any specified value of $[OEt^-]$. Figure 2 shows a typical curve obtained in this way for 2,4-dinitrodiphenylamine. The fact that this curve is, indeed, a straight line provides further evidence that Beer's law is actually obeyed by the solutions in question and, accordingly, that the band widths employed were sufficiently narrow. The failure of the line to pass through the origin indicates that the reference cell and the working cell were not exactly matched; it does not affect the linearity of the curve, however. A similar straight line, which always contained at least four experimental points, was obtained for each concentration of sodium ethoxide used with each of the acids studied. The slopes of these various lines, from which were calculated the values of the apparent extinction coefficients k' at the corresponding concentrations of ethoxide ion, were determined by the method of least squares. The values of $1/k'$ for 2,4-dinitroaniline are plotted in Fig. 3 as a function of [NaOEt].

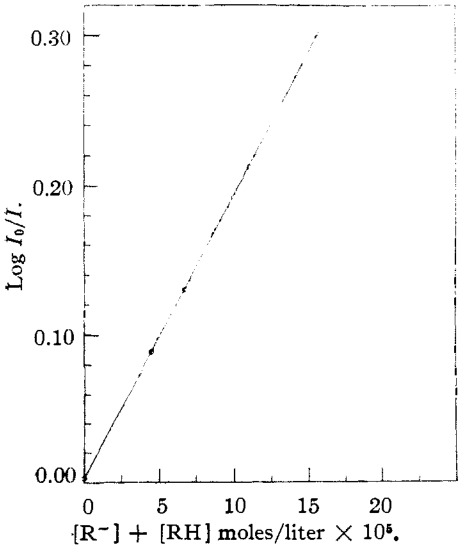

Fig. 2.—Optical density of solutions of 2,4-dinitrodiphenylamine in sodium ethoxide: [NaOEt] is 2.832×10^{-2} mole/liter.

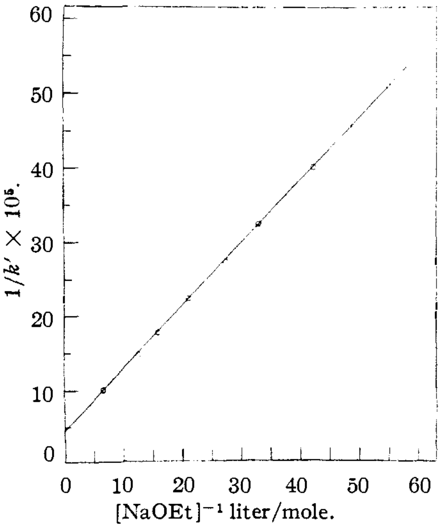

Fig. 3.—Apparent extinction coefficient of 2,4-dinitroaniline in sodium ethoxide solutions at 25°.

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[6] The absorption spectra of these compounds in both neutral and alkaline solutions have been studied by Ramart-Lucas and Grumez, *Compt. rend.*, **211**, 120 (1940).

TABLE I

	k	K_e	K_a	pK_a
4,4′,4″-Trinitrotriphenylmethane in ethanol	2.744×10^4 at 5500 Å.	5.035×10^1	3.66×10^{-18}	17.44
2,4-Dinitrodiphenylamine in ethanol	4.395×10^3 at 5750 Å.	2.668×10^1	1.94×10^{-18}	17.71
2,4-Dinitroaniline in ethanol	2.436×10^3 at 5750 Å.	4.773	3.47×10^{-19}	18.46
4-Nitrodiphenylamine in ethanol	4.380×10^4 at 5750 Å.	3.453×10^{-2}	2.51×10^{-21}	20.6
p-Nitrobenzyl cyanide in water	2.89×10^4 at 4200 Å.	4.00	4.0×10^{-14}	13.4

The sodium salt of 4,4′,4″-trinitrotriphenylmethane is very easily oxidized; elaborate precautions were therefore taken to remove and exclude oxygen from the system and the solutions used. The removal of oxygen was accomplished in the following manner. Approximately 0.5 g. of the stock solution of trinitrotriphenylmethane was weighed into a small tube and sealed to one leg of an inverted Y tube. To this same leg was sealed a vacuum absorption cell. The solvent was removed from the sample by evaporation *in vacuo*. To the second leg of the inverted Y tube was sealed a calibrated flask with a graduated neck. This tube contained a known volume of standardized sodium ethoxide. Absolute ethanol was placed in a separate reservoir. The dissolved gases were removed from the alcohol and sodium ethoxide by freezing the liquids in liquid nitrogen, evacuating the system, melting the liquids in high vacuum and then refreezing and remelting until all the dissolved gas had been removed.

The alcohol in the reservoir was then distilled into the calibrated tube. The "inverted Y" tube was then sealed off from the vacuum line, and the solution in the calibrated flask was allowed to come to 25.0°, and the volume was recorded. The total volume of the system and concentration of sodium ethoxide were therefore known. The tube was then inverted so that the solvent could come in contact with the trinitrotriphenylmethane in the side tube. The contents were well mixed, and the absorption cell was filled and sealed off. It was necessary for the above operation to be carried out in very high vacuum and for all the traces of oxygen and peroxide to be removed from the ethanol; otherwise the blue methide ion would be destroyed and the values of optical density would be in error. Solutions of 4,4′,4″-trinitrotriphenylmethane are colorless, and the methide ion is a deep blue.[7] The spectrophotometric measurements could therefore be made at the maximum in the absorption band of the methide ion. This procedure gave a high precision in the values of k' and it was not necessary to make a series of measurements at a given ethoxide concentration as in the previous cases, although it was now necessary, of course, to correct for the above-mentioned differences between the reference and working cell. The experimental data are plotted in Fig. 4.

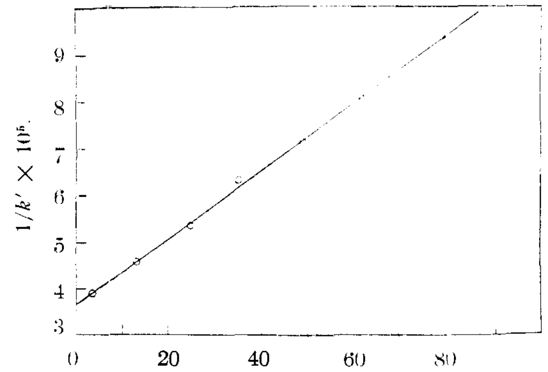

Fig. 4.—Apparent extinction coefficient of 4,4′,4″-trinitrotriphenylmethane in sodium ethoxide solutions at 25°.

p-Nitrobenzyl cyanide in aqueous solutions at a *p*H below 11 is yellow; at a higher *p*H it begins to turn red.[8] It was hoped that the ionization constant of this compound could be determined both in water and in ethanol. Unfortunately, the compound is unstable in alkaline solutions. The color in alkaline solutions changes from red to green, the rate increasing with the concentration of base. An approximate value of the ionization constant in water was obtained by making extremely rapid measurements. Values of log I_0/I were obtained in less than a minute after the base was added. For this purpose a Lumetron colorimeter Model 400 was employed. This instrument contains a barrier layer type of cell and gives readings of the optical density directly in log I_0/I to two figures. Approximately monochromatic light is achieved by the use of glass filters. In spite of the fact that the light was not monochromatic, Beer's law apparently was obeyed. The rate of decomposition in alcohol was found to be much more rapid than in water, and therefore no values were obtained in this solvent.

Results

In Table I the value of the extinction coefficient, k, of the equilibrium constant, K_e, of the ionization constant K_a and of pK_a, all at 25°, are tabulated for 4,4′,4″-trinitrotriphenylmethane, 2,4-dinitrodiphenylamine, 2,4-dinitroaniline, 4-nitrodiphenylamine in ethanol and for *p*-nitrobenzyl cyanide in water.

As is obvious from equation 8, the stronger the acid, the smaller will be the slope of the line obtained by plotting $1/k'$ against $1/[OEt^-]$. And, conversely with a weak acid the slope of the line will be very large. Thus, in the case of 4-nitrodiphenylamine, the extrapolation of the "best" line appears to go almost through the origin. The value of the dissociation constant for this compound is therefore less accurate than those for the other compounds.

For high concentrations of base in the case of 2,4-dinitroaniline it was found that the linear relation between $1/k'$ and $1/[OEt^-]$ fails. This is probably because the approximations made in the development of equation 8 fail to apply in concentrated solutions.

Analysis of the data shows that for ionization constants between 10^{-16} and 10^{-19} the precision obtained is of the order of 2%. The accuracy estimated by comparison of pK_a values obtained at several different wave lengths is of the order of 10%.

In a discussion of 4,4′,4″-trinitrotriphenylmethide ion as a secondary base, Lewis[9] gives data from which the pK_a of the acid can be estimated to be 17.1. This value is in agreement with our value.

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[7] A. Hantzsch and F. Hein, *Ber.*, **52**, 493 (1919).

[8] Spitzer, *Ann. Chim. Applicata*, **29**, 219 (1939).

[9] G. N. Lewis and G. T. Seaborg, THIS JOURNAL, **61**, 1894 (1939).

Theoretically, the compounds described here can be used as indicators. With the knowledge of the value of the equilibrium constant and of the concentration of indicator, the concentration of base can be calculated from measured values of I_0/I. From these data, the ionization constants of colorless compounds may be found. Benzamide, *p*-nitrobenzamide, lauryl mercaptan and glycerol were added to solutions of 2,4-dinitrodiphenylamine of constant ethoxide concentration in an attempt to determine their dissociation constants. Benzamide had no effect on the value of k' and has therefore a pK_a greater than 20. *p*-Nitrobenzamide shows a small effect on the value of k' and the pK_a may be estimated to be about 19. Lauryl mercaptan on the other hand is too strong an acid to be measured by this method, and must have a pK_a less than 15. The pK_a of glycerol was found to be 18.4 in ethanol. The titration curve is shown in Fig. 5.

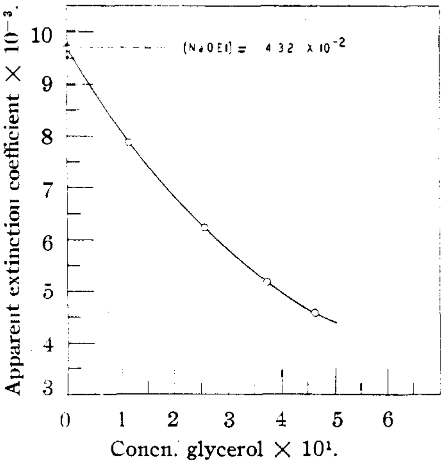

Fig. 5.—Use of 2,4-dinitrodiphenylamine as an indicator at 5000 Å. to determine the dissociation constant of glycerol in ethanol.

Summary

A precise spectrophotometric method is described whereby the ionization constants of weak acids may be determined provided there is a shift in the absorption maximum on ionization. The ionization constants of 4,4',4''-trinitrotriphenylmethane, 2,4-dinitrodiphenylamine, 2,4-dinitroaniline, 4-nitrodiphenylamine and glycerol in alcohol, and of *p*-nitrobenzyl cyanide in water were determined.

CHICAGO, ILLINOIS RECEIVED MARCH 20, 1947

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Observations on the Stability of the Barium–Hydrogen and Zirconium–Hydrogen Systems[1]

BY W. C. SCHUMB,[1a] E. F. SEWELL[1a] AND A. S. EISENSTEIN[1b]

Introduction.—The need for quantitative information about the formation and thermal dissociation of barium hydride arose during the development of the hydrogen thyratron[2] in the Radiation Laboratory, Massachusetts Institute of Technology. A major problem encountered in this development was the maintenance within certain limits of an adequate hydrogen pressure in the tube, and a primary cause of loss of hydrogen pressure was found to be the formation of barium hydride as free barium was liberated from the oxide cathode. As indicated below, the literature contained only fragmentary data on the dissociation pressures of barium hydride at various temperatures and the present investigation was undertaken to supply the desired information. In addition, it was decided to measure the equilibrium gas pressures in the zirconium–hydrogen system, for which some earlier data were available, as this hydride gave promise of use as a hydrogen reservoir, when employed with an auxiliary temperature control circuit.

Observations on the Barium-Hydrogen System.—Aside from the early work of Guntz[3] and of Gautier[4] on the interaction of hydrogen with barium amalgam[3] or with barium–cadmium alloy,[4] and the later observations of Dafert and Miklauz[5] on the preparation of barium hydride from hydrogen and metallic barium (reduced from the oxide by aluminum powder), the only careful study of the dissociation of barium hydride appears to be that of Ephraim and Michel,[6] who employed metallic barium prepared from the oxide by reduction with excess of magnesium.

Guntz[3] had reported the reaction of barium and hydrogen to be far from complete at 1200°, he therefore heated several hundred degrees higher; Gautier[4] found absorption of hydrogen to be noticeable even at 350°; while Dafert and Miklauz[5] observed absorption of hydrogen by finely divided barium in a heated porcelain tube to begin

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[1] This paper is based on work done for the Office of Scientific Research and Development under Contract OEMsr-262 with the Massachusetts Institute of Technology. The paper was presented at the Hydride Symposium of the Chicago meeting of the American Chemical Society, September 10, 1946.

[1a] Department of Chemistry.

[1b] Radiation Laboratory, now at the Physics Department.

[2] Tube types 3C45, 4C35, 5C22.

[3] Guntz, *Compt. rend.*, **132**, 963 (1901).

[4] Gautier, *ibid.*, **134**, 1109 (1902).

[5] Dafert and Miklauz, *Monatsh.*, **34**, 1685–1712 (1913).

[6] Ephraim and Michel, *Helv. Chim. Acta*, **4**, 900–924 (1921).