Recently Glasgow, Streiff and Rossini[3] have published a method for determining both the freezing point of a sample of a compound and the freezing point of the same compound with zero per cent. impurity from the same time-temperature cooling curve. We have applied this method to the determination of the freezing points of our phthalic anhydride samples.

Temperatures were measured with a Bureau of Standards calibrated platinum resistance thermometer used in conjunction with a White Double Potentiometer. The resistance of the thermometer was checked at the ice-point before and after the work on phthalic anhydride.

The highest freezing point of any sample obtained was 130.97° with several samples freezing at 130.95°. Our average value for the freezing point of phthalic anhydride with zero impurity is 130.95 ± 0.03°. This value is the average of those found for nine different samples of phthalic anhydride.

Our value for the freezing point of pure phthalic anhydride is in much better agreement with the value given by Monroe (130.84°) than with that given by Burriel-Marti (131.60°).

Monroe has also published data for the system phthalic anhydride–phthalic acid. Our value for the freezing point (129.80°), and composition (1.65 mole per cent. phthalic acid), of the eutectic is in fair agreement with the values published by Monroe (129.74° and 1.75 mole per cent. phthalic acid).

---

[3] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Nat. Bur. Standards*, **35**, 355 (1945).

CALIFORNIA RESEARCH CORPORATION
RICHMOND, CALIFORNIA

RECEIVED JUNE 7, 1946

The Variation of Composition of 40:60 Isoprene–Styrene Copolymers with Conversion[1]

BY ELIZABETH DYER AND DOROTHY LEVIS MUNROE[2]

There is little published work dealing with the emulsion copolymerization of isoprene and styrene.[3,4] In ascertaining the effect of varying conditions on the emulsion copolymerization of a 40:60 mixture of isoprene and styrene, an approximately equimolecular mixture, it was observed that the initially formed copolymer contained about 80% of styrene. As the reaction was continued to maximum conversion, the styrene content decreased to approximately 60%. These results show that at this monomer ratio styrene enters the copolymer faster than does isoprene. This behavior is similar to that of styrene when copolymerized with acrylonitrile and with vinylidene chloride.[5] The evidence also indicates that the copolymer is not homogeneous with respect to composition.

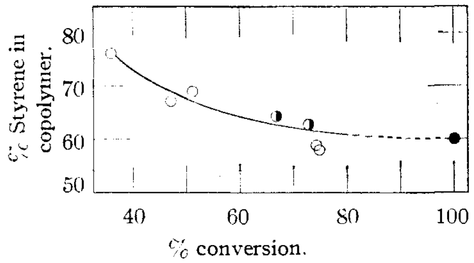

Fig. 1.—Variation of styrene content with degree of conversion: ○, run 20; ◑, run 21; ●, theoretical point.

Procedure.—The most satisfactory polymerization recipe in parts by weight was: isoprene, 40; styrene, 60; water, 200; potassium persulfate, 0.30; sodium oleate, 20; dodecyl mercaptan, 0.25. The experiments were carried out with 10 g. of monomers in 50-ml. test-tubes[6] which had been cleaned with concentrated nitric acid and which were seated on a rotating shaft and turned end over end in an insulated water-bath at 40°.

After agitation for the specified time, the latex was steam distilled to remove unchanged monomers and the polymer was coagulated with 0.6 M hydrochloric acid. The tough, rubbery coagulum was cut into small pieces to facilitate removal of acid, then dissolved in benzene containing phenyl-β-naphthylamine in an amount equal to 2% by weight of the polymer. The benzene solution was dried with calcium chloride, and the polymer further purified by several reprecipitations from benzene and methanol. The removal of most of the solvent prior to analysis was done by the frozen benzene technique.[7] The samples were finally dried to constant weight at 56° and a pressure of about 2 mm.

The conversion was measured by drying a known portion of the acid coagulum to constant weight at 80°.

The composition of the polymer samples in terms of percentage of styrene was determined from their iodine numbers according to the method of Kemp and Peters[8] in which % styrene = 100 − (100 × iodine value/372.6). Results from two runs are shown in Fig. 1. The data of Run 20 were obtained from samples taken after reaction periods of three, eight, thirteen, twenty-one, and twenty-four hours, respectively, while those of Run 21 were from ten and sixteen hour samples.

Acknowledgment.—The authors are indebted to the Armstrong Cork Company for a fellowship in support of this investigation, and to Dr. P. O. Powers, who suggested the problem, for advice and assistance.

---

[1] From the Master's Thesis of Dorothy Levis Munroe, University of Delaware, 1946.

[2] Armstrong Cork Company Research Fellow.

[3] Copolymers of styrene and isoprene were described by Frying at the Atlantic City Meeting of the American Chemical Society, which was held after the completion of this thesis.

[4] Soday, U. S. 2,317,857, April 27, 1943.

[5] Lewis, Mayo and Hulse, THIS JOURNAL, **67**, 1704 (1945).

[6] Fryling, *Ind. Eng. Chem., Anal. Ed.*, **16**, 2 (1944).

[7] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 135 (1945).

[8] Kemp and Peters, *Ind. Eng. Chem., Anal. Ed.*, **15**, 455 (1943).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF DELAWARE
NEWARK, DELAWARE

RECEIVED AUGUST 17, 1946

Ionization Constants of Some Weak Acids in Aqueous Tertiary Butyl Alcohol

BY WILLIAM H. FLETCHER[1]

The objective of the work reported in this paper was to obtain reasonably accurate information regarding the ionization constants of certain mercaptans and alkyl substituted phenols. A review of the literature failed to show any recorded work on the ionization constants of aliphatic mercaptans, although thiophenol and a number of its derivatives have been investigated by Schwarzenbach and Egli,[2] using cells with liquid junctions in 49 and 95% (by vol.) ethanol.

---

[1] Present address: University of Minnesota, Minneapolis, Minn.

[2] Schwarzenbach and Egli, *Helv. Chim. Acta*, **22**, 360 (1939); **17**, 1176 (1934).

In the present work the use of a mixed solvent was necessitated by the very low water-solubility of the compounds to be tested. The use of a glass electrode and cells with liquid junctions in such a solvent makes it impossible, of course, to obtain an exact thermodynamic ionization constant. Comparisons, however, may be made with some confidence. The solvent used in this work was 23.0% (by wt.) aqueous *t*-butyl alcohol.

The glass–calomel electrode combination has been used for similar measurements on substituted phenols by Hodgson and Smith,[3] on dibasic acids by J. C. Speakman,[4] and on halogenated anilines and phenols by Bennett, Brooks and Glasstone.[5] The validity of results obtained with such cells has been discussed by Speakman and by Bennett, Brooks and Glasstone, so those considerations need not be covered here. It is worth noting, however, that Speakman[4] determined *pK* for benzoic acid in 25 and 50% (by wt.) aqueous ethanol and in 30% aqueous dioxane using both the glass–calomel electrode combination and cells without liquid junctions consisting of a quinhydrone electrode and a silver–silver chloride electrode. He found that the *pK* values were from 0.1 to 0.2 unit lower when the cells without liquid junctions were used.

All reagents were obtained commercially, and were either carefully fractionated or were recrystallized several times from a suitable solvent. Water having a specific conductance of 1 × 10^{-6} was used for preparing solutions.

The ionization constants were determined by making *p*H measurements on the following cell, using a Beckman model G *p*H meter and external electrodes.

$$\begin{array}{c|c||c|c} \text{Glass} & \text{HA, NaA,} & \text{Agar-satd.} & \text{Calomel} \\ \text{electrode} & t\text{-BuOH}(23.0\%\ \text{by wt.}),\ \text{H}_2\text{O}\ (77.0\%) & \text{KCl bridge} & \text{electrode} \end{array}$$

A rather rapid change in junction potential took place when the calomel electrode was immersed directly in the butanol solution, but when an agar-saturated potassium chloride bridge was used no drift was observed. For measurements on thiophenol the low *p*H glass electrode (type 1190) was used, but in all other instances the high *p*H electrode (type 1190E) was employed.

Solutions of the phenols or mercaptans were made up immediately before use and were titrated with five or six suitable increments of 0.01860 *N* carbonate-free sodium hydroxide. (The sodium hydroxide solution was also made up in 23.0% aqueous *t*-butyl alcohol.) After the first addition, equilibrium was established very quickly and the readings remained constant for at least fifteen minutes. All determinations were carried out at 25.0 ± 0.05° using a mechanically regulated water-bath.

The ionization constants were calculated in terms of concentrations, using the equation

$$K = [\text{H}^+][\text{A}^-]/[\text{HA}] \qquad \text{(I)}$$

No attempt was made to correct these concentrations to activities as the magnitude of the corrections is well within the uncertainties of the method employed.

In order to make corrections for hydrolysis of the A^- ion, an approximation to the ion product of water in the solvent used was obtained by referring to the work of Akerlof[6] and the work of Harned[7] and his associates. It was assumed that the degree of ionization of a weak acid is largely a function of the dielectric constant of the solvent. Other factors, such as solvation and the activity of the water in the solution used, were necessarily neglected. The dielectric constant of the solvent used in this work was determined by interpolation from a plot of the data of Akerlof[6] on aqueous solutions of *t*-butyl alcohol. The data of Harned and Fallon[7] on the variation of the ion product of water in aqueous dioxane solutions was plotted, and by interpolating from it, one can obtain a fair value of the ion product of water at any dielectric constant down to about 20. Then, assuming that the ion product of water will be the same in aqueous *t*-butyl alcohol as in aqueous dioxane of the same dielectric constant, the value of k_w at 25° in 23.0% *t*-butyl alcohol was found to be 2.3 × 10^{-15}. The dielectric constant of this solution is 58.6 at 25°. This assumption would probably lead to serious errors at low dielectric constants, but in the solvent used in the present work the dielectric constant is high enough that the error is small. The mole fractions of *t*-butyl alcohol and dioxane in solutions of that dielectric constant are nearly the same, and so the activity of the water will not differ appreciably in the two solutions.

In calculating the ionization constant of thiophenol, the value of $[\text{A}^-]$ in equation (I) was taken to be equal to the concentration of sodium hydroxide added. Hydrolysis in this case is negligible, but with the weaker acids the hydrolysis of A^- is appreciable and the corrections were calculated using 2.3 × 10^{-15} for k_w.

TABLE I

A. Ionization constants in 23.0% aqueous *t*-butyl alcohol at 25°

Acid	No. of detns.	*pK′*
Thiophenol	9	7.47 ± 0.01
Phenol	12	10.79 ± .02
p-Methoxyphenol	12	10.96 ± .01
p-*t*-Butylphenol	15	11.11 ± .02
p-Cyclohexylphenol	12	11.20 ± .02
n-Butyl mercaptan	14	11.51 ± .02
n-Octyl mercaptan	13	11.72 ± .02
B. Ionization constants in pure water at 25°		
Phenol	12	9.94 ± .01
p-Methoxyphenol	16	10.16 ± .02

---

(3) Hodgson and Smith, *J. Chem. Soc.*, 263 (1939).

(4) J. C. Speakman, *ibid.*, 270 (1943).

(5) Bennett, Brooks and Glasstone, *ibid.*, 1821 (1935).

(6) G. Akerlof, THIS JOURNAL, **54**, 4125 (1932).

(7) Harned and Fallon, *ibid.*, **61**, 2374 (1939).

Table I gives a summary of results in pK'. Concentrations were expressed in moles per liter and the range was 0.0018 to 0.0035 molar. K' for phenol and for *p*-methoxyphenol was determined by the same procedure in pure water in order to provide a comparison of degree of dissociation in the two solvents. These results are given in Part B of Table I. The concentration range used in pure water was 0.002 to 0.005 molar.

THE CHEMICAL RESEARCH LABORATORIES
THE LUBRIZOL CORP.
CLEVELAND, OHIO
RECEIVED SEPTEMBER 21, 1946

The Determination of Silicon in Relatively Nonvolatile Organosilicon Compounds

BY H. GILMAN, R. N. CLARK, R. E. WILEY AND H. DIEHL

In connection with a study of organosilicon compounds a need arose for a rapid and precise method of analysis for silicon. The general procedures for the analysis of silicon in organosilicon compounds have involved the oxidative decomposition of such types to silicon dioxide. The reagents used have been fuming nitric acid,[1] a combination of pyrolysis and atmospheric oxidation,[2] sulfuric acid and potassium permanganate,[3] concentrated sulfuric acid,[4] and sodium peroxide in the Parr bomb fusion procedure of Schumb and co-workers,[5] which is broadly useful for all types of organosilicon compounds.

We have found that heating with 60% perchloric acid is a rapid and accurate procedure for the quantitative conversion of silicon in relatively non-volatile organosilicon compounds to silicon dioxide. A modification of this method which may be useful for some compounds which oxidize very easily is to use a nitric acid–perchloric acid mixture. Mixtures containing nitric acid have been used for the quantitative analysis of tin in organotin[6a] compounds, and for lead in organolead[6b] compounds. The general use of perchloric acid for the destruction of organic matter, alone and mixed with nitric acid or sulfuric acid, has been reviewed recently by Smith.[7] Attention is called specifically to the fact that 60% perchloric acid is used in the procedure now described rather than the 72% acid. The oxidation potential of the acid is thus kept relatively low at the start and increased gradually as the temperature is raised and the acid concentrated. The oxidation of organic matter then proceeds smoothly and with a minimum of carbonization.

Experimental

Procedure (A).—About 0.2 g. of the organosilicon compound is weighed out in a platinum crucible, and then 5 cc. of 60% perchloric acid is added. The crucible and contents are placed in a clay triangle supported on a porcelain casserole; this air-bath is then heated with the full flame of a Meker burner until all of the acid has evaporated and all fumes of perchloric acid have disappeared. The crucible is then ignited to constant weight. The total time required, including initial weighing of sample and final weighing of silicon dioxide, is about three hours. It was shown, in several control analyses, that the precipitate formed by ignition is silicon dioxide by treatment in a customary manner with sulfuric and hydrofluoric acids and weighing the empty crucible. In some fifty analyses there was no violent action using the perchloric acid method of oxidation. When many determinations are to be made attention should be paid to the hazard resulting from the condensation of perchloric acid on combustible flues. Wood saturated with perchlorates burns vigorously and has even produced explosions when heated. A simple device to circumvent this difficulty is a so-called miniature laboratory fume eradicator.[8]

Procedure (B).—The only essential difference between this method and Procedure (A) is the admixture of 2 cc. of concentrated nitric acid with the 5 cc. of 60% perchloric acid. During the initial application of heat there may be foaming with this mixture but this can be corrected by reducing the heat or removing the burner until the foaming subsides. The foaming sometimes leaves a ring of froth near the top of the crucible. When this happens, the froth can be washed down with about 3 cc. of 60% perchloric acid after the initial evaporation. Then the mixture is again evaporated to dryness.

The results of a few representative analyses are given.

TABLE I

RESULTS OF ANALYSES

Compound	Procedure	% Si Calcd.	% Si Found	
Tetraphenylsilane	A	8.35	8.31	8.37
	B		8.30	8.36
Triphenylsilanol	A	10.23	10.24	10.29
	B		10.21	10.16
Methyltriphenylsilane	B	10.22	10.20	10.27
p-Carboxyphenyltrimethylsilane	A	14.43	14.29	
Triphenyl-2-thienylsilane	A	8.19	8.19	

Acknowledgment.—The authors are grateful to R. A. Benkeser for assistance.

---

(1) Friedel and Crafts, *Ann.*, **136**, 203 (1865).

(2) See, Polis, *Ber.*, **19**, 1024 (1886) for an account of the procedure by Ladenburg.

(3) Polis, *ibid.*, **18**, 1540 (1885).

(4) Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

(5) Marvin and Schumb, THIS JOURNAL, **52**, 574 (1930); Schumb, Ackermann, and Saffer, *ibid.*, **60**, 2486 (1938). See, also Tseng and Chao, *Science Repts. Natl. Univ. Peking*, **1**, (No. 4) 21 (1936) [*C. A.*, **31**, 655 (1937)]; Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 801 (1938); and Whitmore and co-workers, *ibid.*, **68**, 480 (1946).

(6) (a) Gilman and King, THIS JOURNAL, **51**, 1213 (1929); (b) Gilman and Robinson, *ibid.*, **50**, 1714 (1928).

(7) Smith, *Ind. Eng. Chem., Anal. Ed.*, **18**, 257 (1946).

(8) Smith, *Monthly Rev. Am. Electroplater's Soc.*, **32**, 1028 (1945).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA
RECEIVED JULY 9, 1946

Acid-Catalyzed Alkylation of Isoparaffins with Alcohols

BY J. D. GIBSON, R. C. COLE AND M. P. MATUSZAK

Tables I and II summarize data obtained several years ago in experiments on the acid-catalyzed alkylation of isoparaffins with alcohols. *t*-Butyl alcohol reacted readily at room temperature; *i*-propyl alcohol, at 50°; *n*-butyl alcohol, not even at 50°.