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An Extraction Method for the Determination of Acids and its Application to Para-Hydroxybenzoic Acid

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Introduction

During a kinetic investigation on the saponification of acetylated hydroxy acids,^{1,2} there arose the rather complex analytical problem of determining a comparatively weak acid ($K \cong 10^{-9.4}$) in a mixture of several stronger acids ($K \cong 10^{-5}$). Various indicator and potentiometric titration methods having been found inapplicable to the compounds under investigation, the possibilities of an indirect extraction method were investigated. Although quantitatively exact only under the conditions indicated by the following equations and rather tedious in actual practice, the method has yielded reproducible results where the simple titration methods failed, and consequently should be of value in similar cases.

The method, in principle, is to determine an acid (HA) in aqueous solution by adding a definite volume of standard alkali in excess of that required to neutralize the acid. The excess alkali is then determined by adding a known weight of a second acid (HE) (in excess of the alkali), extracting the excess of HE with a solvent in which HA is insoluble, and subsequently determining the extracted excess of HE by the usual methods. Knowing the excess of HE, and from this, the amount of excess alkali present, one may calculate by difference the amount of alkali combined with HA.

- (1) La Mer and Greenspan, *THIS JOURNAL*, **56**, 1492 (1934).
(2) Greenspan, Thesis, Columbia University, June, 1933.

The necessity for such a procedure arises in the determination of *p*- and *m*-hydroxybenzoic acids. It has been known for a long time³⁻¹¹ that these acids, in contrast to the ortho acid (salicylic), cannot be determined quantitatively as monobasic acids by alkali titration with phenolphthalein as indicator, the color change appearing after the stoichiometric end-point, and in addition being very indefinite.

For example, we obtained the following results in a series of titrations. 0.5430 gram of *p*-hydroxybenzoic acid dissolved in 100 cc. (0.039 *M*) of water containing 2 drops of 1% phenolphthalein indicator was titrated with 0.2914 *M* sodium hydroxide. Found: 16.17 cc. where first indistinct color appeared, with very gradual change in color to 17.5 cc. Calculated: 13.50 cc.

0.6249 grams of *m*-hydroxybenzoic acid: first color change at 16.44 and gradual to 16.7. Calcd.: 15.54.

The discrepancies are not due to carbon dioxide as shown by blanks containing water and indicator. The results were even more discordant for the more dilute solutions encountered in our rate measurements.

In a recent paper, Osol and Kilpatrick¹² report the solubilities of these two acids in salt solutions

- (3) Kellas, *Z. physik. Chem.*, **24**, 239 (1897).
(4) Walker and Wood, *J. Chem. Soc.*, **73**, 618 (1898).
(5) Kailan, *Monatsh.*, **28**, 116 (1907).
(6) Thiel and Roemer, *Z. physik. Chem.*, **63**, 744 (1908).
(7) Sidgwick, *J. Chem. Soc.*, **117**, 402 (1920).
(8) Kolthoff, *Z. anorg. Chem.*, **112**, 188 (1920).
(9) Larsson, *ibid.*, **183**, 35 (1929).
(10) Allen, *Trans. Faraday Soc.*, **26**, 528 (1930).
(11) Kaplan, *Ber.*, **63**, 1589 (1930).
(12) Osol and Kilpatrick, *THIS JOURNAL*, **55**, 4440 (1933).

to an accuracy of 0.2% (private communication from Dr. Osol) using phenolphthalein, but give neither the details of their procedure nor mention of any analytical difficulties. Since their findings are in direct contradiction to the results of many investigators, including ourselves, we await publication of the details of their method with much interest.¹³

Attempts to employ mixed indicators in the pH range 6–8.4 yielded correct results for certain mixtures of *p*-hydroxybenzoic and acetic acids, but failed when the ratio of these two acids was altered.¹⁴ Nile Blue indicator (pH 10–11), suggested by Kaplan¹¹ to titrate the para acid as a dibasic acid is out of the question here since the acetoxy acids also present in our mixtures are unstable in alkaline solution.

A differential electrometric titration¹⁵ with hydrogen electrodes gave a curve without definite inflection points. Larsson⁹ has found a similar result.

Kolthoff⁸ titrated the *p*-hydroxybenzoic acid conductometrically in 60% alcoholic solutions and reported two breaks in his titration curve, the first being difficult to estimate. A repetition of these titrations in aqueous solution ($\cong 0.04$ Molar vs. $\cong 0.25$ M NaOH) by Mr. Silvester Liotta in this Laboratory showed that both inflection points could be estimated and yielded results determined directly from the plot within 1% of theory. Such titrations could not be used in our velocity measurements because of the time required for each titration and because of the presence of other acids.

The Extraction Method.—Chloroform was chosen as extracting medium since *p*-hydroxybenzoic acid ($K_1 \cong 10^{-5}$, $K_2 \cong 10^{-9}$) is insoluble in this solvent. Cinnamic acid was selected as the titrating acid, since it is soluble in chloroform but not in water and is of the appropriate strength, *i. e.*, $K \cong 10^{-6}$. In the ideal case, the cinnamic acid should neutralize the excess alkali in the

(13) Pearce and Newsome in an abstract mention measurements on the solubilities of these acids, but no data or details of procedure are available [Pearce and Newsome, *Proc. Iowa Acad. Sci.*, **38**, 163–164 (1931)].

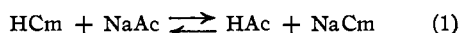
(14) The kinetic problem involves a solution initially containing only *p*-acetoxybenzoic acid (titration exponent, $P_T \sim 8.0$) and subsequently various mixtures of this acid and a 1:1 ratio of *p*-hydroxybenzoic and acetic acids, the exact composition being a function of time. Kolthoff (see forthcoming paper) calculates $P_T = 6.8$ for the hydroxy acid and $P_T = 6.95$ for the equimolecular mixture of *p*-hydroxy and acetic acids. Since the P_T shifts during the progress of the saponification reaction, different indicator end-points are required.

(15) MacInnes and Cowperthwaite, *THIS JOURNAL*, **53**, 555 (1931).

aqueous solution, replace the alkali used up by the phenolic group ($K \cong 10^{-9}$) but none of the sodium hydroxide used in neutralizing the carboxy group ($K \cong 10^{-5}$) in the hydroxybenzoic acid. The extent to which these conditions may be realized in practice depends on all the equilibria involved, *i. e.*, those dependent on the concentrations, distribution coefficients and dissociation constants of the compounds.

Experiments 4 and 3, below, show how well *p*-hydroxybenzoic acid fulfils the necessary conditions. At a ratio of 1 mole of the acid to 2 moles alkali (concn. = 0.01561 M/l.) the titer value was only 0.4% para acid less than originally added; however, when the mole ratio was made 1:1 (concn. = 0.03122 M/l.), the value became 3.4% lower than calculated. Since Expt. 4 closely approximated the conditions (as regards *p*-hydroxybenzoic acid) found in our rate measurements, we have a quantitative method for determining *p*-hydroxybenzoic acid as a monobasic acid when these experimental conditions are adhered to.

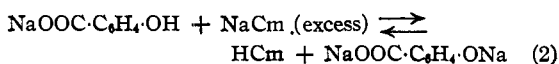
Such was not the case for acetic acid (also present in our rate measurements). Experiment 5 shows that when a sodium acetate solution (0.03481 M), just pink to phenolphthalein, was extracted with a chloroform solution of cinnamic acid, only 93% of the calculated cinnamic acid was recovered. This may be due to the increased solubility of cinnamic acid in sodium acetate solution (as compared to solubility in water) or it may arise because the two compounds enter into the equilibrium



Since acetic and cinnamic acids have different distribution coefficients, in general one mole of acetic acid would not enter the chloroform layer for each mole of cinnamic acid involved in the above equilibrium of the aqueous layer and the result would be low titer values—which is the case. Further, if equilibrium (1) were really the cause of the low values, it should be possible to displace it to the left by addition of excess sodium cinnamate so that little free acetic acid would be formed. In Expt. 7 we find that the cinnamic acid is now quantitatively recovered, and hence acetic acid can be determined.

It should now be noticed that the use of excess sodium cinnamate to hinder formation of free acetic acid will likewise hinder formation of the free phenolic group in *p*-hydroxybenzoic acid.

Thus, excess sodium cinnamate will displace the equilibrium



to the right with formation of a disodium salt to an extent depending on the relative dissociation constants of the three acidic groups involved and the relative concentrations. Such an effect is, of course, undesirable here; it would cause a higher titer value than calculated for *p*-hydroxybenzoic acid, since cinnamic acid formed by equilibrium (2) would be extracted by the chloroform. Experiments 9 and 10 show that such is actually the case, giving values $\cong 5\%$ too high.

As equilibrium (2) indicates, a decrease in concentration of phenolic acid or sodium cinnamate or the use of an acid with a *K* higher than cinnamic would tend to diminish such errors. We have developed the general equations which permit calculation of the experimental conditions requisite for successful use of this method and have illustrated their application for the mixtures of four acidic groups present in our rate measurements.

Theory

Given.—A mixture of four acids, *A* moles of HA, *B* moles HB, *C* moles HC, *D* moles HD in a volume of water, *V*₁, where *A*, *B*, *C*, *D* are unknown.

Problem.—To find *A* + *B* + *C* + *D* by adding *Z* moles of sodium hydroxide (*Z* being larger than *A* + *B* + *C* + *D*), followed by *Y* moles of HE and μ moles of NaE and *V*₂ cc. of CHCl₃ and then titrating the amount of HE (= *q*) extracted by the CHCl₃.

Known.—The dissociation constants, *K*_A, *K*_B, etc., and the distribution coefficients *D*_A, *D*_B, . . ., of the acids; the volumes *V*₁ (includes volume of added NaOH, *Z* moles) and *V*₂; the quantities *Z*, *Y*, *q* + (*m* + *n* + *o* + *p*, see below) and μ .

Steps I, II, III represent diagrammatically the equilibria present at various stages in the pro-

cedure. Two conditions must be true of the process as a whole: (1) One equivalent of sodium salt must be formed for each mole of sodium hydroxide which is neutralized. (2) One equivalent of acid must be neutralized by each mole of sodium hydroxide which is used up.

Employing condition 1 in going from I to III, we get

$$\underbrace{Z - l}_{\text{I}} = - \underbrace{[0 - (\alpha + \beta + \gamma + \delta + \epsilon - \mu)]}_{\text{III}} \quad (3)$$

Loss in NaOH Gain in Na salts

μ being subtracted since it is not formed in the neutralization process.

Using condition 2 for transition from II to III

$$\underbrace{x - l}_{\text{II}} = \underbrace{(a_1 + a_1' + b_1 + b_1' + c_1 + c_1' + d_1 + d_1' + Y)}_{\text{III}} - \underbrace{\mu}_{\text{II}}$$

Loss in NaOH

$$\underbrace{(a + a' + m + b + b' + n + c + c' + o + d + d' + p + e + e' + q)}_{\text{III}} \quad (4)$$

Loss in acid

By making the appropriate mathematical transformations, one secures the following relationships

$$h \cong r q \frac{K_A V_1^2 D_A}{V_2(\alpha + \alpha')} \cong r q \frac{K_B V_1^2 D_B}{V_2(\beta + \beta')} \cong r q \frac{K_C V_1^2 D_C}{V_2(\gamma + \gamma')} \cong r q \frac{K_D V_1^2 D_D}{V_2(\delta + \delta')} \quad (5)$$

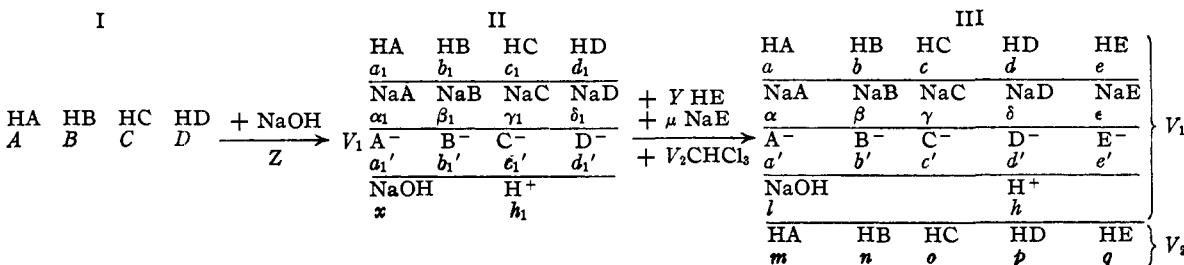
which must be satisfied in order to make *m*, *n*, *o*, and *p* each $\leq r q$, where *r* is a very small fraction (*i. e.*, *r q* is negligible compared to *q*). But

$$h = K_E V_1 e / \epsilon + e' \quad (6)$$

and since *h* can be made any value (mathematically) by changing ϵ (*i. e.*, amount of sodium cinnamate), we can satisfy the condition. If *r q* is to equal zero, then *h* must equal zero, which can be obtained by making ϵ (*i. e.*, $\cong \mu$) infinite. The practical limit on *h* is, of course, the concentration of H⁺ in a saturated solution of NaE.

We shall apply this equation to our own mixtures, assuming one extraction with CHCl₃.

HA = acetoxybenzoic acid, $K \cong 10^{-6}$, $D \cong 10^{-1}$, $(\alpha + \alpha') = 10^{-3}$
 HB = COOH group in *p*-hydroxybenzoic acid, $K \cong 10^{-6}$, $D \cong 10^2$, $(\beta + \beta') = 10^{-3}$



HC = OH group in *p*-hydroxybenzoic acid, $K \cong 10^{-10}$,
 $D \cong 10^2$, $(\alpha + c') = 10^{-3}$, 10^{-6}
 HD = acetic acid, $K \cong 10^{-5}$, $D \cong 1$, $(\delta + d') = 10^{-3}$
 $V_1 = V_2 = 10^2$; we desire $rq \cong 10^{-6}$, where $q \cong 10^{-3}$
 or an accuracy of 0.1%.

In each of these four cases, we solve for h through equation (5), assuming each acid independent of the others; $h = 10^{-7}$ for HA, 10^{-4} for HB, $10^{-9} \rightarrow 10^{-6}$ for HC (using $10^{-3} \rightarrow 10^{-6}$ for $(\gamma + c')$) and 10^{-6} for HD. To satisfy the most unfavorable case, $h = 10^{-9}$ (*i. e.*, where all the OH group exists as ONa), substitute in (6) remembering $K_E \cong 10^{-5}$, $e = D_E q = 10^{-2} \times 10^{-3} = 10^{-5}$, $\epsilon + e' \cong \mu$. We see that $\mu \cong 10$ in order to make $h = 10^{-9}$ or 10 moles sodium cinnamate per 100 cc. must be present to convert all the OH group to ONa by equilibrium (2), a condition which must be absent for the success of this procedure.

To drive (2) completely to the left, *i. e.*, $h \cong 10^{-6}$ or $\mu \cong 0.01$. In order to get all of the acetic acid in the form of NaAc, *i. e.*, $h = 10^{-6}$, μ must be approximately 10^{-2} or the addition of 0.01 mole NaCm will drive equilibrium (1) to the left. Thus, the addition of 0.01 mole of NaCm to our solution should simultaneously keep all the acetic acid in the form of sodium acetate and all the phenolic group in the unneutralized form, and should permit quantitative determination of the *p*-hydroxybenzoic acid. In the presence of HA, $\mu = 10^{-1}$, and HC, $\mu = 10^{-4}$, so that theoretically μ should be between 0.0001 and -0.1 . In our experiments we have employed $\mu \cong 0.01$ mole with the results discussed above.

Purification of Materials

***p*-Hydroxybenzoic Acid.**—Commercial material twice recrystallized from water-alcohol mixture, using norite, dried over sulfuric acid *in vacuo* for twenty-four hours¹⁶ and heated at 103° for six hours,¹⁷ m. p. 214.2-214.7° corr.

Cinnamic Acid.—Recrystallized from benzene, air dried for two days, oven dried at 86° for three hours, m. p. 134° uncorr.

Chloroform.—Commercial material washed with sodium carbonate solution, then water; dried over sodium sulfate or calcium chloride; fractionated, collecting fraction 60-63° uncorr.

***n*-Propyl Alcohol.**—Commercial, fractionated from sodium hydroxide solution, collecting fraction at 94-97° uncorr.

Sodium Propylate Solution (approximately 0.03 *M*).—Prepared by dissolving 0.6 g. of sodium in 1 liter of *n*-propyl

alcohol. Standardized against standard sulfuric acid, phenolphthalein indicator. Blank correction was determined by using same volume of alcohol and same indicator. The solution held its titer within 0.2% for one week, when kept in a well-ground glass-stoppered bottle.

Sodium Cinnamate.—Commercial material twice recrystallized from water (+ norite first time).

Procedure

The desired amount of standardized aqueous alkali and sufficient water to make the total volume 50 cc. were placed in a 250-cc. pear-shaped separatory funnel, and then a definite amount of *p*-hydroxybenzoic acid was added in a small platinum thimble. By means of a special addition tube,¹⁸ a weighed amount of cinnamic acid was then added and washed down with 50 cc. of chloroform. This mixture was shaken, allowed to stand for several minutes and the chloroform layer drawn off into a flask. Another 50 cc. of chloroform was added to the aqueous layer and the extraction repeated. The combined chloroform extracts were then titrated directly with standard sodium propylate solution with phenolphthalein indicator. The precipitate of sodium cinnamate formed during titration provides an excellent background for securing the very sharp and reproducible end-point in chloroform solution.

To correct for losses caused by the solubility of cinnamic acid in water, or sodium cinnamate solution, or for impurities of materials, the appropriate blanks were first determined, using 50 cc. of water (or 50 cc. of water + 1 g. of sodium cinnamate) as the aqueous layer and the same quantities of cinnamic acid + chloroform; the appropriate corrections were applied in the determinations.

All the results reported below are the averages of at least two separate determinations whose maximum deviation was never more than 0.4% and usually much better.

Experimental Results

1. **Blank on Solvents and Titration Error.**—100 cc. of CHCl_3 + 35 cc. of propyl alcohol; titrate with approximately 0.03 *M* sodium propylate. Required: 0.34 cc. of sodium propylate.

2. **Blank on Extraction Error.**—Aqueous layer: 50 cc. of water; added 0.1559 g. of cinnamic acid; extract twice with 50 cc. of chloroform; titrate with 0.03008 *M* sodium propylate. Found: 34.78 - 0.34 = 34.44 cc. of sodium propylate.

This extraction procedure was followed in all the succeeding experiments.

3. **0.03122 *M* *p*-Hydroxybenzoic Acid** (acid:alkali::1:1 mole).—Aqueous layer: 0.2154 g. of *p*-hydroxybenzoic acid + 50.00 cc. of 0.03121 *M* sodium hydroxide; 0.1559 g. of cinnamic acid used. Found: 33.62 - 0.34 = 33.28 cc. Calculated from 2: 34.44 cc.

4. **0.01561 *M* *p*-Hydroxybenzoic Acid** (acid:alkali::1:2 moles).—As in 3, except that 0.1077 g. of *p*-hydroxybenzoic acid was used. Found: 8.93 cc. Calculated: 9.04 cc. % deviation = $100 \times (9.04 - 8.93)/(34.44 - 9.04) \cong 0.4\%$.

5. **Sodium Acetate in Absence of Sodium Cinnamate.**—Aqueous layer: 50 cc. of 0.03481 *M* Na acetate solution. Found: 31.92 cc. of sodium propylate. Calculated from 2: 34.44 cc.

(16) Kolbe, *J. prakt. Chem.*, [2] 10, 98 (1874).

(17) Barth, *Ann.*, 152, 96 (1869).

(18) Greenspan, *This Journal*, 56, 2053 (1934).

6a. **Blank on Extraction in Absence of Sodium Cinnamate.**—Same as 2, but different standard alkali and 0.1684 g. of cinnamic acid used. Found: 34.92 cc. of 0.03250 *M* sodium propylate.

6b. **Blank on Extraction in Presence of Sodium Cinnamate.**—Same as 6a, except 1.000 g. of sodium cinnamate added. Found: 34.26 cc.

7. **Sodium Acetate in Presence of Sodium Cinnamate.**—Same as 5, except 1.000 g. of sodium cinnamate added. Found: 34.14 cc. Calculated from 6b: 34.26.

8. **Blank on Extraction in Presence of Sodium Cinnamate.**—Same as 6b, except 0.03008 *M* sodium propylate and 0.1559 g. of cinnamic acid used. Found: 33.80 cc.

9. **0.03122 *M* *p*-Hydroxybenzoic Acid in Presence of Sodium Cinnamate.**—Same as 3, except 1.000 g. of sodium cinnamate added. Found: 35.57 cc. Calculated from 8: 33.80 cc.

10. **0.01561 *M* *p*-Hydroxybenzoic Acid in Presence of Sodium Cinnamate.**—Same as 4, except 1.000 g. of sodium cinnamate added. Found: 10.05 cc. Calculated: 8.87 cc. % deviation = $100 \times (10.05 - 8.87)/(33.80 - 8.87) = 5.0\%$.

We wish to express our thanks to Professor J. J. Beaver for permission to use the conductiv-

ity apparatus and to Mr. S. Liotta for performing the conductivity titrations.

Summary

1. A general theory for the quantitative determination of an acid (or base) by extraction with buffers has been developed.

2. The method has been applied to the determination of *p*-hydroxybenzoic acid in dilute solution, an acid which is not amenable to direct titration using phenolphthalein as indicator.

3. The limits of the method have been calculated theoretically for mixtures of various acids and determined experimentally for *p*-hydroxybenzoic acid in the presence of acetic acid.

4. The titration of cinnamic acid in chloroform solution with sodium propylate has yielded highly reproducible and sharp end-points in dilute solution (approximately 0.03 *M* alkali *vs.* 0.005 *M* acid) with phenolphthalein indicator.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Acidimetric Titration of *p*-Hydroxybenzoic Acid Alone and in the Presence of Acetic Acid

By I. M. KOLTHOFF

p-Hydroxybenzoic acid is a dibasic acid, the first ionization constant¹ at 19° being equal to 3.3×10^{-6} and the second to 4.8×10^{-10} .¹ The ratio of the two constants is about 100,000 and therefore it may be expected² that *p*-hydroxybenzoic acid can be determined as a monobasic acid if the titration is carried out until the proper titration exponent is reached. The *pH* at the first equivalence point can be calculated² from the first and second ionization constants and is equal to $\log \sqrt{K_1 K_2}$ or $1/2 (pK_1 + pK_2) = 6.90$. The above ionization constants refer to infinitely dilute solutions in which the activities of the various ions and undissociated acid are equal to 1. For the present purpose it is preferable to calculate the titration exponent from the concentration constants. The latter again were calculated from the colorimetrically determined *pH* during the neutralization of 0.035 molar aqueous solution of *p*-hydroxybenzoic acid and were found to be equal to $K_1 = 4.5 \times 10^{-6}$ and $K_2 = 5.6 \times$

10^{-10} , corresponding to a *pH* at the first equivalence point of $1/2 (4.35 + 9.25) = 6.8$. The titration of *p*-hydroxybenzoic acid as a monobasic acid should give good results with brom thymol blue or phenol red as indicators, with the use of a buffer with a *pH* of 6.8 containing the same amount of indicator and having the same volume as the solution to be titrated at the end-point, as a comparison solution. Experimentally this was shown to be the case. About 0.3 g. of pure *p*-hydroxybenzoic acid was dissolved in about 50 ml. of warm water; the solution was cooled to room temperature and titrated with

TABLE I

TITRATION OF *p*-HYDROXYBENZOIC ACID TO *pH* = 6.8

<i>p</i> -Hydroxybenzoic acid taken, g.	Water, ml.	0.1 N sodium hydroxide used, ml.	<i>p</i> -Hydroxybenzoic acid found, g.	Deviation, %
0.3004	50	21.86	0.3016	+0.4
.2996	70	21.79	.3006	+ .3
.3001	70	21.81	.3009	+ .3
.3013	50	21.89	.3020	+ .2
.3014	50	21.91	.3023	+ .3
Average deviation				+0.3

(1) R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 1 (1928).

(2) See I. M. Kolthoff, "Volumetric Analysis, I," translated by N. H. Furman, John Wiley and Sons, Inc., New York, 1931, p. 57.