

THE ACIDITY OF FORMALDEHYDE AND THE END-POINT IN THE FORMOL TITRATION

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Two factors are involved in a systematization of the formol titration. The first of these factors is the titration constant of the amino acid in formaldehyde solution. This aspect has been discussed in a previous paper (4) for certain of the monoamino acids. The basic amino acids will be treated later. The second factor is the behavior of the solvent on the addition of strong alkali, just as the behavior of water in the same condition must be considered in the titration of weak acids. The present paper describes the titration of formaldehyde solutions with strong alkali and contains a discussion of the application of the data to the formol titration.

The acidity of commercial formalin is often ascribed to the presence of carboxylic acids, particularly formic acid, as impurities. Simple observations of the color changes of phenolphthalein in the titration of formalin with alkali show a distinct buffering power in its range (8.4 to 10) where carboxylic acids do not buffer. The same behavior is shown by pure formaldehyde solutions which do not contain carboxylic acids. It is evident that formaldehyde is itself a sufficiently strong acid to account for a measurable amount of alkali at the concentrations used in the formol titration.

The quantitative aspect of the reaction with alkali is dependent on the dissociation constant of the aldehyde and the determination of this constant should lead to useful formulations for calculating the alkali bound by formaldehyde, if this be desirable. In addition, the accuracy of the titration of amino acids is largely determined by the sharpness of the end-point, or by the steepness of the titration curves near the end-point. This in turn depends on the relative amounts of alkali bound by the amino acid and

by the solvent. The data can therefore be used to show the most favorable conditions for accurate titration and the inherent limitations of the system as a quantitative method.

Euler and Euler (2) estimated a first dissociation constant of formaldehyde at about 10^{-14} and believed that they had evidence for a second dissociating H ion. Their estimate was based on a

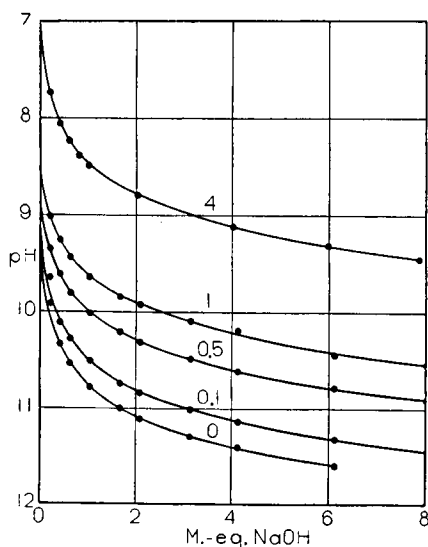


FIG. 1. The titration curves of formaldehyde at various concentrations. Ordinate pH; abscissa NaOH added in milli-equivalents per liter. The figure above each curve gives the formaldehyde concentration in moles per liter.

comparison of the freezing points of alkali-formaldehyde mixtures with those of urea-nitric acid mixtures and the dissociation constants of urea given by Walker and Wood (8). The actual concentrations of formaldehyde were determined from freezing points rather than by analysis. The experiments may be taken as demonstrating a reaction between alkali and formaldehyde but the constant is not accurate.

EXPERIMENTAL

The experimental details have been previously described in part (4). 0.1 N HCl was used to standardize the calomel cell with

−0.0647 volt as the potential of the H electrode in this solution (1). An exactly known volume of formaldehyde solution (approximately 10 ml.), containing 0.02 M NaCl to stabilize the activity coefficients and provide conductivity, was prepared in the electrode vessel. It was titrated with 0.2 N NaOH. The titration curves obtained are shown in Fig. 1 and certain of the data are given in detail in Table I. No correction was made for liquid junction potential. The temperature was 30°.

Calculation of Constants—The titration of formaldehyde at constant concentration follows the Henderson-Hasselbalch equation.

$$(1) \quad \text{pH} = \text{pK}'_f + \log \frac{[\text{CHO}^-]}{[\text{CH}_2\text{O}]}$$

pK'_f is an apparent constant because concentrations (indicated by brackets) are used instead of activities. If $[\text{B}^+]$ is the concentration of total alkali added, $[\text{CHO}^-] = [\text{B}^+] - [\text{OH}^-]$ from the principle of electroneutrality. But $[\text{OH}^-] = \gamma_{\text{OH}} K_w / (\text{H}^+)$ where γ_{OH} is the activity coefficient of OH^- and the parentheses indicate activities. Therefore

$$(2) \quad \text{pH} = \text{pK}'_f + \log \frac{[\text{B}^+] - (\gamma_{\text{OH}} K_w / (\text{H}^+))}{[\text{CH}_2\text{O}]}$$

γ_{OH} was calculated from the ionic strength, μ , by the equation given on p. 500 of Clark (1) with the constants at 30°.

$$(3) \quad -\log \gamma_{\text{OH}} = 0.509 \sqrt{\mu} / (1 + 0.329 \sqrt{\mu})$$

μ varied only between 0.02 and 0.03. Equation 3 is a result of the Debye-Hückel theory of electrolyte solutions and contains as one factor the dielectric constant of the medium. No data have been found in the literature on the dielectric constants of formaldehyde solutions. Therefore, the value for water has been assumed to hold. Certain typical data are given in Table I to facilitate correction, if necessary, when the appropriate dielectric constants become known. The data have been selected so that the pK'_f calculated from each is equal to the average for the titration it represents. The range of pK'_f at a single formaldehyde concentration is ± 0.03 unit.

The value of pK_w used in the calculations was 13.85. This was obtained with the present set-up for the titration of 0.02 M NaCl in water with NaOH. Harned and Hamer (3) obtain the value 13.83 from cells without liquid junction. The higher value was used because it probably carries systematic errors which also affect the other measurements. In particular no correction for liquid junction potential was made.

The values of pK'_f given in Column 5 of Table I vary with the formaldehyde concentration, F . By plotting pK'_f against F a straight line is obtained whose slope is -0.19 . The titration data can therefore be represented so as to be independent of F by the

TABLE I
Titration of Formaldehyde at 30°. Representative Data

[B'] (1)	[F] (2)	pH (3)	μ (4)	pK'_f (5)	$pK'_f + 0.19F$ (6)
<i>M</i>	<i>M</i>		<i>equivalent</i>		
0.00313	0.102	11.01	0.0234	12.86	12.88
0.00412	0.505	10.61	0.0243	12.77	12.87
0.00167	1.02	9.83	0.0221	12.65	12.84
0.00402	3.99	9.12	0.0239	12.12	12.88
Average.....					12.87

use of Equation 4 in which pK''_f may be called a "reduced" constant and is the titration constant at $F = 0$.

$$(4) \quad pK'_f = pK''_f - 0.19 F$$

Column 6 gives the values of pK'_f calculated by this relation. The average value is 12.87.

Since the results are affected by uncertainties as to the activity coefficients of ions, neglect of liquid junction potential, and probably by an unconsidered variation of the activity coefficient of formaldehyde with concentration, the significance of Equation 4 is not immediately evident. This uncertainty does not invalidate its use in the discussion of the end-point below.

End-Point in Formol Titration—An understanding of the limitations and conditions of a quantitative method can be reached only by an intensive study of the principles on which the method

depends. The accumulated data are now adequate for a discussion of certain practical aspects of the formol titration.

The titration may be divided into two steps. First the solution to be analyzed is adjusted to some preliminary pH where, it is hoped, the amino acids have the potentiality of reacting with 1 further equivalent of alkali per amino group on the addition of formaldehyde. This preliminary adjustment has usually been to pH 7. The discussion of Van Slyke and Kirk (7) shows how it affects the titration.

In the second step of the titration formaldehyde is added and the addition of alkali continued to some alkaline end-point. This end-point has been chosen by trial and error (6). Usually the titration is corrected for a blank with formaldehyde alone. In the discussion the conditions for the second step of the titration will be considered.

These conditions are similar to those for the titration of a weak acid with a strong alkali in water discussed by Roller (5) except that the behavior of both the solvent and the amino acid depends on the formaldehyde concentration. For the special case of a weak acid titrated with alkali Roller's equation for the percentage error is

$$(5) \quad E = \pm 200 \sqrt{K_w/C_A K_A} \sinh. \Delta$$

K_w has the usual significance but it may be generalized as an index of the behavior of the solvent on the addition of strong alkali. It may be called the solvent constant. A function will be derived which gives exactly analogous information about the behavior of the solvent in the formol titration. This function can be substituted for K_w in Equation 5. K_A is the dissociation constant of the weak acid. In the formol system it is to be replaced by G_f , the dissociation constant of the amino acid at a particular formaldehyde concentration (4). C_A is the molar concentration of the amino acid at the end-point.

By the colorimetric method $\Delta = \pm 2.3\Delta\text{pH}$. The last term is the finite sensitivity of the indicator. With the use of a buffer standard for comparison $\Delta\text{pH} = \pm 0.1$ unit and $\Delta = \pm 0.23$. For small values of Δ such as this, $\sinh. \Delta$ is practically equal to Δ .

Function in Formol Titration Corresponding to K_w —If it be remembered that F in the formol titration is high (2 to 10 M),

certain simplifications of Equation 2 may be made. Thus $[\text{CH}_2\text{O}]$ is approximately constant and equal to F . $[\text{OH}^-]$ is small compared to $[\text{CHO}^-]$. Then

$$(6) \quad \text{pH} - \log [\text{CHO}^-] = \text{pK}'_f - \log F = \text{pK}''_f - 0.19 F - \log F$$

$-\log [\text{CHO}^-]$ corresponds to pOH of an aqueous system. It is the result of the solvent acting as an acid. The reciprocal of the antilogarithm of the last part of Equation 6 therefore corresponds to K_w of Roller's equation when the formol titration is considered. Its value is $K''_f F \times 10^{0.19F}$

Function in Formol Titration Corresponding to K_A —In a previous paper (4) an equation was derived which was valid at high F (2 to 7 M) for the amino acids considered there, except proline.

$$(7) \quad \text{pG}_f = -\log K_2 L_2 - 2 \log F$$

pG_f is the titration constant of the amino acid at formaldehyde concentration F and K_2 is the alkaline dissociation constant of the amino acid in water. L_2 is the association constant of the amino acid anion with 2 molecules of formaldehyde.¹

The reciprocal of the antilogarithm of pG_f may be substituted for K_A in Equation 5.

$$(8) \quad G_f = K_2 L_2 F^2$$

For proline the corresponding constant is $K_2 L_1 F$.

Most Favorable Formaldehyde Concentration—Replacing K_A and K_w of Equation 5 with the analogous formol functions and putting $\Delta\text{pH} = \pm 0.1$, an expression for the error in the formol titration at the stoichiometric point is obtained.

$$(9) \quad E = \pm 46 \sqrt{(K''_f \times 10^{0.19F}) / C_A K_2 L_2 F}$$

By differentiating with respect to F and setting the derivative equal to 0, a minimum value of E can be demonstrated at $F = 2.29 \text{ M}$ (6.9 per cent). This minimum is not very sharp and a range of formaldehyde concentrations, 2 to 3 M or more, gives practically identical values of E . The result of these calcula-

¹ The nomenclature of the constants has been changed as may be noted by comparison with Equation 12 of a previous paper (4). K_2 is the former K_1 and L_2 is the former K_3 . The change is in the interest of clarity.

tions is the definite recommendation that the formaldehyde concentration at the end of the formol titration should be between 6 and 9 per cent.

Stoichiometric End-Point, pH_s .—Roller has shown that E is smallest when the end-point is at the stoichiometric point. This is defined as the pH of the solution containing equivalent quantities of the acid and alkali. It corresponds to $[H^+] = \sqrt{K_w K_A / C_A}$. In the formol titration it is given by

$$(10) \quad pH_s = \frac{1}{2} (-\log K_2 L_2 + pK''_f - 0.19 F - 3 \log F + \log C_A)$$

The constant $-\log K_2 L_2$ varies for the different amino acids. In dealing with a mixture of amino acids it is necessary to choose some average value for the calculation of the end-point. 7.9 appears to be a fair approximation. With F at 2.3 M, $pH_s = 9.6 + \frac{1}{2} \log C_A$. pH_s is more sensitive to F than is E . The wrong value of pH_s leads to a constant error in one direction or another. The range of F which changes pH_s by 0.1 unit is 2.1 to 2.7 M. This is another reason for controlling the formaldehyde concentration between 2 and 3 M. For a 0.1 M amino acid at the end volume, the proper end-point is pH 9.1. Of course, if one is dealing with a single amino acid, the best end-point can be calculated by the use of Equation 10 and the proper constants.

Is a blank desirable? The titration of commercial formalin can be divided into that part due to impurities and a second part due to the acidity of formaldehyde. If the commercial formalin is neutralized to pH 7 the first part of the blank is eliminated. For the second part, which would be titrated from pH 7 to the end-point, it is not desirable to make a correction. pH_s is by definition the pH at which the solution contains equivalent quantities of alkali and amino acid. If the titer of the formaldehyde alone were subtracted from the total titer to pH_s , the result would be too low by just the amount equivalent to the blank. If a more alkaline end-point than pH_s were used, the correct titer would be the total titer minus the blank between pH_s and the end-point, not the total blank. As Roller points out the net error of the titration corresponding to the finite sensitivity of the indicator is least at pH_s because the rate of change of pH is a maximum at this point and the error consequently a minimum.

The error of the formol titration will therefore be greater if it is run to a more alkaline end-point than indicated by Equation 10 and corrected for the blank, even if the proper correction is made. If initially neutral formaldehyde is used, a blank is not desirable.

Amino Acid Concentration—Equation 9 shows that the error is reduced by increasing amino acid concentration. Consequently the amino acid should be at as large a concentration as possible at the end of the titration. The principle that diluting fluids such as the formol added should be as concentrated as possible should be adhered to. The concentration of alkali solution should be as great as is consistent with the measuring instruments employed.

Proline—This substance does not follow the equations given because its anion is apparently capable of reacting with only 1 molecule of formaldehyde. By substituting the function K_2L_1F in Equation 5 no practical minimum of E is found with F ; E diminishes constantly as F increases. pH_s at 2.3 M is $9.9 + \frac{1}{2}\log C_A$. In the presence of large amounts of proline as in gelatin hydrolysates the end-point of the formol titration should be somewhat more alkaline than otherwise.

Intrinsic Error of Formol Titration—When the most favorable conditions for the formol titration have been set up, Equation 9 can be used to calculate the intrinsic error of the titration. For the monoamino acids other than proline, E under the specified conditions is $0.165/\sqrt{C_A}$. If C_A is 0.1 M, E is 0.5 per cent. With the more alkaline end-point calculated in the last section, E for proline is $0.37/\sqrt{C_A}$. If C_A is 0.1 M, E is 1.2 per cent. These errors are in addition to any errors in the preliminary adjustment of the amino acids. Practically, they represent the errors to be expected when titrating from the isoelectric points of monoamino-monocarboxylic acids.

Indicator—Indicator tints are not always reliable as pH indices especially when the standard buffer and the unknown differ greatly in composition. All of the discussion has been based on hydrogen electrode measurements. If the conclusions are to be of practical use, it is necessary to show that the indicator color is not disturbed by the presence of formaldehyde in the concentration recommended. To show this, formaldehyde solution containing phenolphthalein was titrated with alkali to the tint in a buffer at pH 9.2. The amount of alkali required was compared with that

calculated by Equation 6 which is based on electrometric data. Below 3.5 M formaldehyde, the alkali required was identical, within the error of titration, with that calculated. This agreement shows that the color of phenolphthalein is the same in water and in formaldehyde at the same pH. Phenolphthalein is therefore suited for use in the formol titration under the conditions described.

SUMMARY

The titration constant of formaldehyde follows the equation $pK' = 12.87 - 0.19F$ at 30°. Deduction from the data at hand indicates that the maximum accuracy of the formol titration is obtained when the formaldehyde concentration is 6 to 9 per cent at the end volume, neutral (pH 7) formalin is used, no correction for a blank is made, the amino acids are at as high a concentration as possible, and the end-point fulfils the specifications to be found in the text.

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