

bons in expts. 9 and 12 were determined with a mass spectrometer by E. C. Kerr.

Acknowledgments.—The authors are indebted to Drs. D. R. Jackson and D. M. Young for assistance in securing much of the experimental data; to Dr. Young for aid in preparing the paper; and to Dr. G. O. Curme, Jr., and Dr. G. A. Perkins for helpful criticisms and suggestions.

Summary

The catalytic removal of oxygen from certain

aldehydes and ketones by means of an alcohol is described. An olefin is produced from the aldehyde or ketone, water is formed, and an aldehyde or a ketone is obtained from the alcohol. Evidence is advanced to show that the deoxygenation of crotonaldehyde is responsible for the formation of butadiene from acetaldehyde and ethanol in the Ostromisslensky reaction. A new synthesis for styrene, involving the catalytic deoxygenation of acetophenone by ethanol, is also described.

SOUTH CHARLESTON, W. VA. RECEIVED JULY 22, 1946

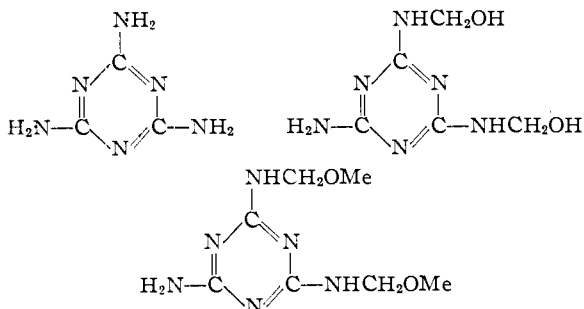
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The Dissociation Constants of Melamine and Certain of its Compounds

By J. K. DIXON, N. T. WOODBERRY AND G. W. COSTA

Introduction

Melamine is a weak base which can be made up into several interesting series of condensation products also of basic character. Two of such series are the methylol melamines and methylated methylol compounds which are illustrated by the formulas



In connection with studies of the formation of polymeric materials from the methylol and methylated methylol melamines, it was of interest to determine the basic dissociation constants of several of these compounds so as to permit correlation of these data with their chemical structures and their properties as polymers. Unpublished information from this Laboratory¹ suggests qualitatively that an increase in the number of methylol groups or in the degree of etherification tends to decrease the rate of polymerization of the monomer. The hydrogen ion concentration is a factor in controlling the rate of polymerization and consequently the basicity of the polymerizing melamine compound affects the acidity of its solution, and, therefore, in turn influences the rate of polymer formation. Although the exact course and mechanism of polymerization are not known, it is expected that the information submitted below will be of help in future interpretations of other experimental data.

(1) J. R. Dudley and J. E. Lynn, *J. Soc. Dyers Colourists*, to be published.

This paper presents measurements of the basic dissociation constants of melamine and certain of its related compounds as determined by electrometric titration and by ultraviolet absorption methods.

Experimental

Preparation of Materials.—The following preparation for methylated trimethylol melamine illustrates methods of preparing methylol and methylated methylol melamines. A mole of melamine was added to sufficient 37–40% formalin (adjusted to a pH 8 with sodium hydroxide) to contain 3.3 moles of formaldehyde. The mixture was heated to 75° with good agitation to complete solution and reaction with formaldehyde over a total time of around half an hour. The solution cleared up after reaction and was then cooled and poured out on shallow trays in order to “crystallize” the trimethylol melamine as a solid cake. The latter was dried at 50° for twelve hours, the low temperature being desirable to prevent extensive polymer formation. This solid product was essentially trimethylol melamine containing but a small fraction of polymerized product. Variations in the ratio of formaldehyde to melamine produced desired differences in the degree of methylation.

In order to convert a methylol compound to its methyl ether, it was dispersed in two times its weight of anhydrous methanol. About 0.5% of oxalic acid, based on the weight of methylol melamine, was added to the slurry and the stirred mixture raised to reflux temperature over a period of twenty minutes. Refluxing was continued for about one hour to dissolve unreacted methylol melamine, after which the reaction mixture was clear and reaction was essentially complete. The pH was adjusted to 9, the solution filtered after the addition of filter aid, and the filtrate evaporated in vacuum at 85–90°. The sirup contained essentially monomeric methylated trimethylol melamine.

Crystalline types of methylol melamine are prepared by following the procedure outlined above, but in addition, working at slightly greater dilution. The crystalline product could be filtered off and washed with acetone. The procedure of Widmer² was followed in order to produce crystalline hexamethyl ether of hexamethylol melamine.

The melamine compounds were analyzed for combined formaldehyde, degree of methylation of the methylol groups, nitrogen and solid content. The nitrogen content determined agreed to within ±2% of that calculated from the molecular weight, using formaldehyde and meth-

(2) Gams, Widmer and Fisch, *Helv. Chim. Acta*, **24**, 302E (1941).

TABLE I
SUMMARY OF DATA ON DISSOCIATION CONSTANTS OF MELAMINE COMPOUNDS, 25 = 3°

Compound	Identifica- tion	Moles HCHO/ moles melamine	% Meth- ylation	Mol. wt.	% N obs.	Titra- tion	pK_b^b		K_s sp. ^a extn. coeff.	
							U. V.	Acidic	Basic	
Melamine	1	0	0	126	66.67	9.0	8.9	73	10	
Dimethylol melamine	180G	1.99	0	185	43.1	9.2	9.5	70	17	
Dimethylol melamine	410B	2.29	0	195	...	9.6	
Trimethylol melamine	410A	3.00	0	216	...	10.1	
Trimethylol melamine	OPR1001	2.97	0	215	...	9.9	9.9	62	14	
Methylated trinitrolyl melamine	A-2	3.17	70	252	...	10.4	10.4	74	21	
Methylated pentamethylol melamine	A-5	4.52	79	312	26.77	10.9	11.5	66	18	
Methylated pentamethylol melamine	S-2	5.00	74	328	...	11.0	
Methylated pentamethylol melamine	L-1	5.35	79	346	23.90	11.8	12.0	62	17	
Methylated hexamethylol melamine	401C	6.00	95	386	...	12.3	11.8	44	14	

^a Concentration in g. per liter; length in cm., K_s is for curve maximum a 4150 mm.⁻¹. ^b $pK_a = 14.0 - pK_b$ at 25°.

ylation data to compute the molecular weight. Table I, which is presented below, summarizes essential analytical data.

pH Measurements.—Samples for pH titrations were prepared at 1% or at 0.25% concentration by weight by dissolving an appropriate amount of melamine compound in distilled water. In most cases the compound was easily soluble, but in a few instances it was necessary to apply heat to produce complete solution. One can, of course, effect easy solution by addition of acid, but this complicates the titration and subsequent calculations. By using acid to obtain solution, a comparison was made with a preparation effected by heating and thus it was shown that the heating period had no essential effect on the titration results as compared with those obtained by solution in acid. There was some indication of slight polymerization on heating as deduced from the titration curves, but this had no effect on results to be presented.

Titrations of the resin solutions were carried out at 23 = 1° with standard 0.1 *N* hydrochloric acid using a Leeds and Northrup pH meter and the usual glass electrode *vs.* calomel half cell. Temperature corrections were made. Calculations are based on hydrogen ion concentrations and not activities. The electrode was standardized with commercial buffer solutions having pH values of 4.0, 7.0 and 10.0.

Ultraviolet Absorption Measurements.—Extinction coefficients of aqueous solutions of the compounds were determined in the region from 3500 to 4500 wave numbers (mm.⁻¹) in a Beckman Quartz Spectrophotometer, Type DU, using a water-cooled hydrogen discharge tube as source. The temperature was 25 = 3°.

Results

Determination of pK_b by Titration.—The dissociation of a melamine compound being studied was calculated from its titration curve on the assumption that the compound is a base, R, the hydronium salt of which dissociates in the manner shown



$$pH = pK_w - pK_b + \log \left(\frac{[R_0]}{[H^+]_0 - [H^+]} \right) - 1 \quad (1)$$

where

K_b is the dissociation constant of RHOH

H_0^+ the molar concentration of hydrogen ions initially, for titration of R

H^+ the molar concentration of hydrogen ions as measured

R_0 the sum of the molar concentrations of all melamine compounds at the measured pH³

K_w dissociation constant for water = 10⁻¹⁴ at 25°

(3) C. L. A. Schmidt, "Chemistry of the Amino Acids and Proteins," C. A. Thomas, 1938, Chapter II.

If $\log \left(\frac{R_0}{[H^+]_0 - [H^+]} - 1 \right)$ is plotted against pH, a straight line with unit slope should be obtained, and when the value of the term in parentheses is unity, $pH = pK_w - pK_b$. Figure 1 illustrates the titration curves for a number of the compounds studied.

For a number of the compounds it is evident from Fig. 1 that the logarithmic plots were reasonably straight lines, indicating that the assumptions above were probably correct. In several instances, for example, dimethylol melamine 410B, the curves were convex to the abscissa axis. An analysis of the derivation of equation (1) indicates that there are at least two factors of importance that might lead to marked deviations from a straight line. The first of these might arise from the presence of appreciable amounts of more than one species of compound, each with a different dissociation constant. There is little doubt that some of the preparations contained several species of compounds other than those indicated by the over-all average analytical figures of Table I, especially for the non-crystalline types. Since the plots in Fig. 1 were reasonably straight lines it is likely that in these cases the effect of more than one species was unimportant. It will also be noted below that small variations in degree of methylation or methylation have no large effect on basicity so that lack of complete molecular homogeneity was not expected to be troublesome.

A second source of deviation from a straight line plot might be as follows: one-sixth of the total nitrogen found by analysis would give the value of R_0 in equation (1). R_0 would not be changed appreciably if the nitrogen atoms remained available for proton binding after polymerization. Conductometric titrations were made on several samples and it was found that in these cases the equivalent concentration was only 90–95% of that calculated from nitrogen analysis. Using the conductance value as being more indicative of the correct concentration, then a corrected R_0 was computed which gave a straight line

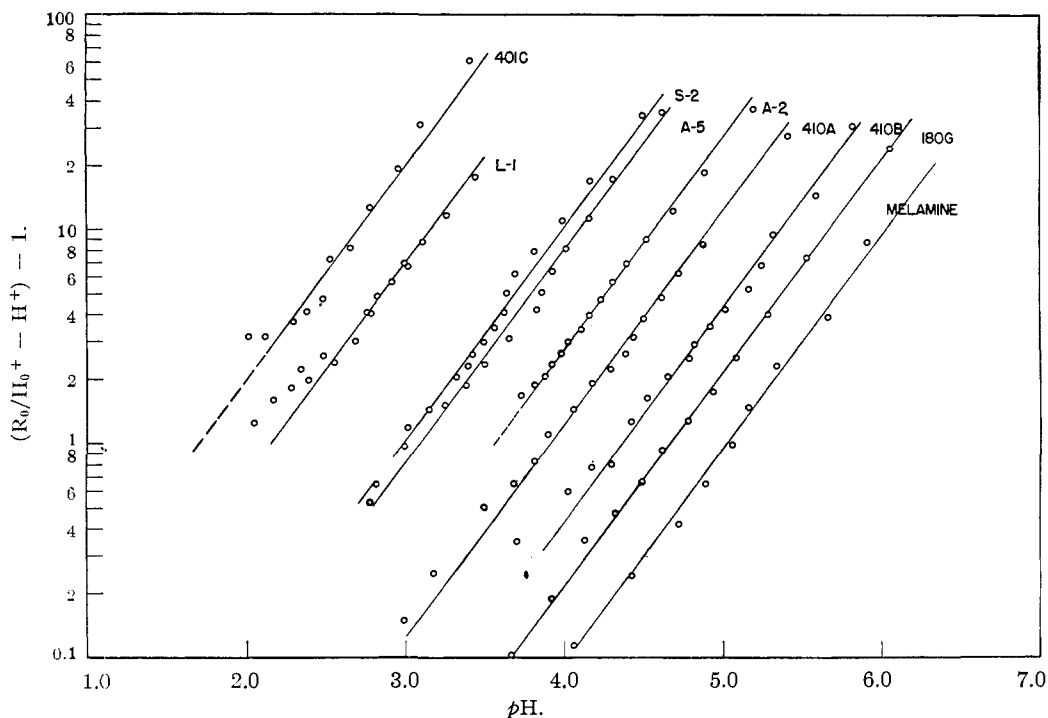


Fig. 1.—Graph used in determination of pK_a 's of melamine and some of its compounds (see text).

plot when used in equation (1). This suggested that possibly because of slight polymerization during preparation, the compounds were not strictly monomeric and that in the polymers some of the nitrogen atoms had become unavailable for proton binding. For some preparations not shown in Fig. 1 the curvature was much too great to be accounted for on the basis of polymer formation; hence it was concluded that species of different pK values were present which led to considerable curvature in the pK plots of the type shown in Fig. 1.

Determination of pK_b by Ultraviolet Spectral Method.⁴—The type of ultraviolet absorption curve obtained for the melamine compounds under investigation is shown in Fig. 2 for three different pH values. The ordinate is the logarithm of the specific extinction coefficient, K_s , where $K_s \times C \times l = \log_{10} I_0/I$ and C = concentration in grams per liter and l = length of absorption cell in cm. The molecular extinction coefficient, K_m , which will be referred to later, is related to K_s by the relation $K_m = K_s \times M$, where M is the molecular weight (always assumed to be monomeric). Although all K values are given for a wave number of 4150 mm.^{-1} , conclusions reached on the bases of K values obtained at 4070 or 4230 mm.^{-1} are the same.

Ultraviolet absorption curves were determined on solutions at concentrations of around 0.4 g. per liter . It will be indicated below that the change in absorption with pH is explained on the

assumption that there are two forms of each melamine compound which absorb in solution. The ratio of the two forms depends on the acidity. At a constant pH , however, the proposed theory requires that the ratio of the two forms be a constant independent of the sum of the concentra-

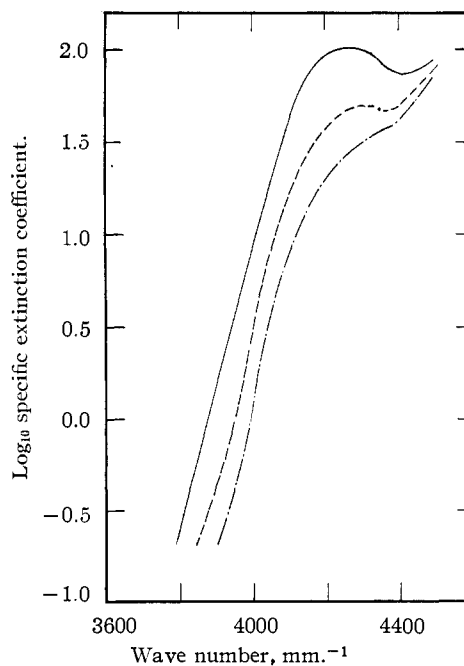


Fig. 2.—UV absorption curves for melamine: — pH 1.96, - - - pH 5.65, - · - · pH 8.46.

(4) See, for example, E. E. Sager, M. R. Schoeley, A. S. Carr and S. F. Acree, *J. Research Bur. Standards*, **35**, 521 (1945).

tions, that is, the total concentration of compound. This means that at constant pH , Beer's law should be obeyed for the mixture if Beer's law holds for each form of the compound. . . Actually at a $pH = 6.15$, measurements on melamine in the concentration range from 0.0213 to 0.200 g. per liter, and on methylated trimethylol melamine resin at 0.0106 to 0.228 g. per liter showed that Beer's law was obeyed exactly. Likewise, at pH 's of 0.8 and 1.6 Beer's law was followed exactly for melamine and trimethylol melamine at concentrations from 0.01 to 0.40 g. per liter. On the basis of these data Beer's law was assumed to be obeyed for all compounds studied in both the high and low pH regions.

From Fig. 2 it is evident that the extinction coefficient varies with pH . One might explain this by assuming one form, say I (see below), adds a proton to give a second form, II. These might be identified with the forms R and RH^+ used in development of equation (1).

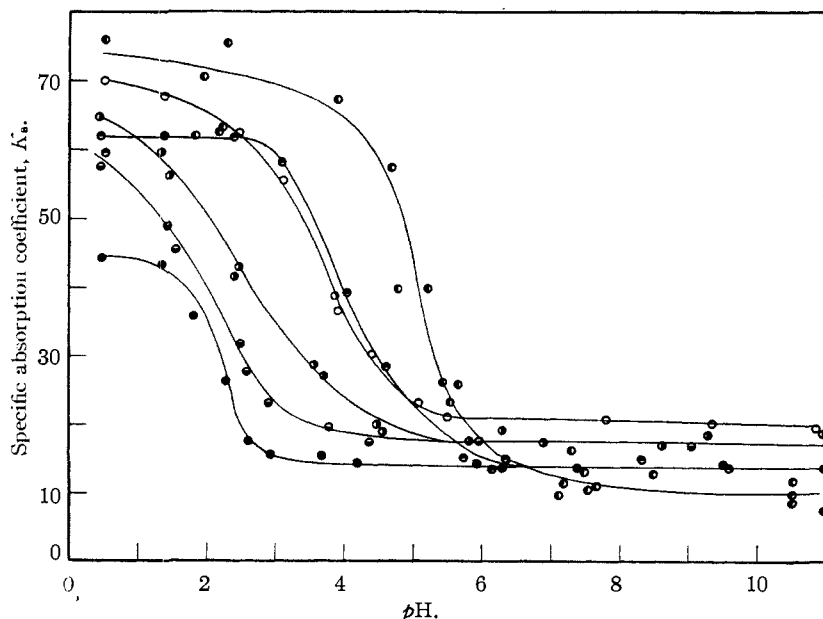
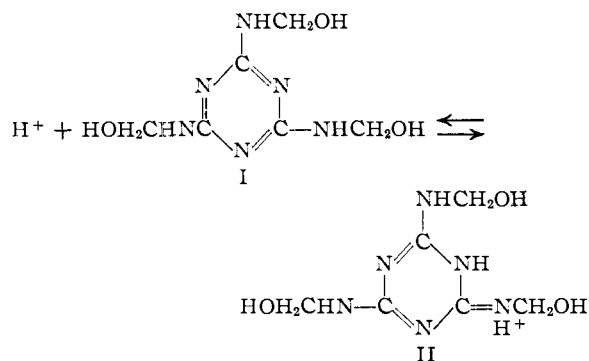
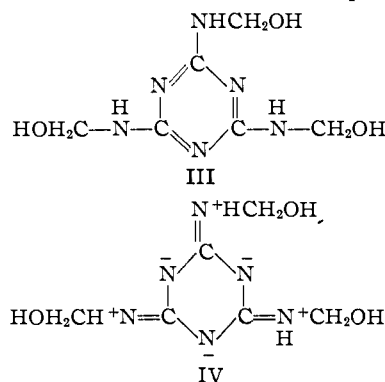


Fig. 3.—Variation of specific absorption coefficient with pH : ● methylated hexamethylmelamine (401C); ○ methylated pentamethylmelamine (L-1); ○ (A-5); ● trimethylol melamine (OPR 1001); ○ methylated trimethylolmelamine (A-2); ● melamine (1).

In this case I would be the "basic" type and II the "acidic" type. On the other hand one might assume several resonance forms,⁵ say I, III and IV. The attachment of a proton would in some manner affect the types and amounts of the various resonating structures, which in turn would influence the absorption spectra.⁶ The forms I, III and IV do not show the attached proton.



In general, it will be assumed that there are two principal forms R and RH^+ and that $RH^+ \rightleftharpoons R + H^+$. If the two structures have different molar extinction coefficients and if $K_a = (R)(H^+)/RH^+$, then it can be shown that pK_a is numerically equal to the pH at which the extinction coefficient is half way between those for the basic and acidic forms.⁴ The value for pK_b is $pK_a - pK_w$. The extinction coefficient is nearly independent of pH above $pH = 7.0$, as it should be if the triazine ring is completely converted to its alkaline form. At low pH values the compound should be all in the acidic form and absorption should be constant, but such was not quite true in some cases. This might have been due to the formation of dihydrochlorides at low pH 's which is excluded from assumptions used to obtain pK_b from Fig. 3. The value of pK_b is, therefore, fixed to within only ± 0.2 unit because of the uncertainty in the extinction coefficient at low pH . Table I summarizes data on the values of K and the pK 's derived therefrom.

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Discussion

From Table I it is evident that the pK_b values by titration and absorption agree reasonably well. This is

(5) Hughes, THIS JOURNAL, 63, 1737 (1941).

(6) G. W. Wheland, "Theory of Resonance," John Wiley & Sons, Inc., New York, N. Y., 1944.

especially true where the compounds are most well-defined, as in the case of melamine, di- and trimethylol melamines. The tri-, penta- and hexa-methylated ether compounds are less likely to be pure compounds, and, therefore, presumably the two procedures lead to different pK_b values because the equations used in calculating them are over-simplified.

The molecular weights and pK 's correlate well as shown in Fig. 4, indicating a linear decrease in basicity as the degree of methylation and/or methylation increases. As regards a comparison

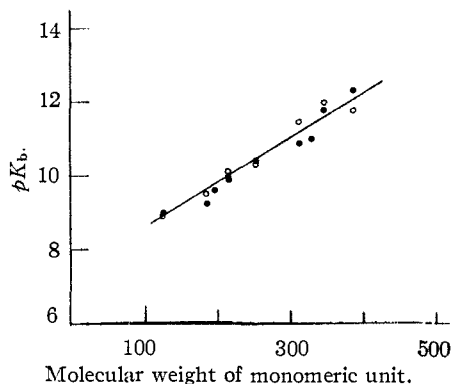


Fig. 4.—Variation on pK_b with the molecular weight of a monomeric unit: ● potentiometric titration data, ○ UV data (see Table I).

of a methylol compound with its ether, a consideration of Table I indicates the etherification of the trimethylol compound increased pK_b from 10.1–9.9 to about 10.4. Other specific data are lacking. It had been hoped that the hexamethylol compound could be titrated for comparison with the corresponding hexa ether. The titration curve for the former was so curved, however, presumably due to the presence of polymers or mixtures of related compounds, that evaluation of pK_b was not permissible. There was indication that pK_b was between 11.2 and 10.2, which is qualitatively in the correct range, since Fig. 4 would predict a value of 11.0.

As the basic form of the compound absorbs protons, its specific extinction coefficient increases as illustrated in Fig. 3. The coefficients, K_s , have been recalculated to a molecular extinction coefficient basis, K_m , and plotted in Fig. 5, thus showing an increase with molecular weight.

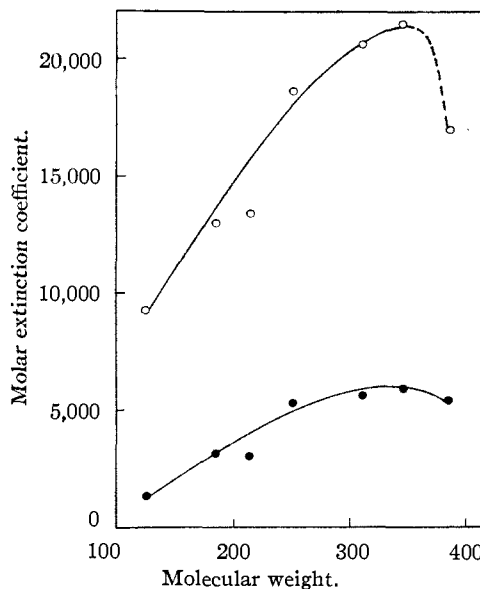


Fig. 5.—Variation of the molar extinction coefficient with the molecular weight of a monomeric unit; ○ acidic, ● basic.

The point for crystalline hexa ether sample is low suggesting a maximum in the acidic extinction coefficient curve. The theoretical interpretation of the variation in absorption with structure is apparently too complicated to warrant discussion here.^{5,6}

Acknowledgment.—Discussions with and suggestions by Drs. D. J. Salley, G. L. M. Christopher and D. Richardson are gratefully acknowledged and thanks are due the Directors of this Laboratory for permission to publish these results.

Summary

The dissociation constants of melamine, several of its methylol compounds and certain of its methylated methylol compounds have been determined by electrometric titration and by means of an ultraviolet absorption spectrum procedure. The basic dissociation constants decreased from 1.1×10^{-9} for melamine to about 1×10^{-12} for the hexamethylated hexamethylol melamines. The value of pK_b varies linearly with the molecular weight of the melamine compound.

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RECEIVED JULY 30, 1946