ages for K_s. The equation for the curve can be obtained immediately from equation (25) and is

$$\bar{n} = 4 - [4(\mathrm{H}^+)^2/K_6K_7(\mathrm{HF})^2 + 3(\mathrm{H}^+)/K_7(\mathrm{HF}) + 2 + K_8(\mathrm{HF})/(\mathrm{H}^+)]K_8(\mathrm{H}^+)^2/(\mathrm{Th}_t^{+4})(\mathrm{HF})^2 \quad (26)$$

Summary

1. The potential of the ferrous–ferric half cell was studied as a function of the hydrofluoric and perchloric acid concentrations, and the data were interpreted by assuming the existence of the ions FeF^{++}, FeF_2^+ and FeF_3. The equilibrium constants for the formation of the above ions has been determined at 25° and an ionic strength of 0.5.

2. The potential of the ferrous–ferric half cell was studied as a function of the hydrofluoric acid and thorium nitrate concentrations, and the data were interpreted by assuming the existence of the ions ThF^{+++}, ThF_2^{++} and ThF_3^+. The equilibrium constants for the formation of these ions and the solubility product of $ThF_4 \cdot 4H_2O$ were determined.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA, AND THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Basic and the Acid Strength of Cacodylic Acid in Water

BY MARY L. KILPATRICK

Zawidzki,[1a] Johnston[1b] and Holmberg[1c] established the fact that cacodylic acid in water is amphoteric, as may be expected from the position it occupies in the series:

H_3AsO_4	arsenic acid
$CH_3AsO(OH)_2$	methylarsenic acid
$(CH_3)_2AsOOH$	cacodylic acid
$(CH_3)_3AsO$	trimethylarsine oxide
$(CH_3)_4AsOH$	tetramethylarsonium hydroxide

where the acid strength decreases from top to bottom.

For the acid strength of cacodylic acid in water

$$K_A = [H_3O^+][(CH_3)_2AsOO^-]/[(CH_3)_2AsOOH]$$

and for the basic strength (then called the hydrolysis constant)

$$K_B = [(CH_3)_2AsOOH \cdot H^+]/[H_3O^+][(CH_3)_2AsOOH]$$

they obtained at 25° the following values: for K_A, 4.2 × 10^{-7}, Zawidzki, by measurement of conductance and application of Ostwald's dilution law; 6.4 × 10^{-7}, Johnston, by measurement of conductance and application of Walker's method for the determination of K_A and K_B for an amphoteric electrolyte; 7.5 × 10^{-7}, Holmberg, by measurement of the rate of decomposition of diazoacetic ester. For K_B, 34, Zawidzki, by measurement of the conductance of solutions containing equivalent amounts of cacodylic and hydrochloric or nitric acid; 32, Johnston, estimated from the conductance data for cacodylic acid, in the manner of Walker; 51, Holmberg, by measurement of the rate of decomposition of diazoacetic ester in solutions containing cacodylic acid and picric or nitric acid. A number of additional values of K_A, but none of K_B, have subsequently been reported; of these, the most reliable appears to be that of Morton,[2] *viz.*, K_A = 5.66 × 10^{-7} at 30°. Morton's determination was made electrometrically with a cell consisting of a hydrogen electrode, a saturated calomel half-cell, and a saturated potassium chloride bridge. The figure 5.66 × 10^{-7} represents the average obtained upon extrapolating to infinite dilution values found with 1:1 cacodylic acid–sodium cacodylate buffer solutions with and without added salt; for acetic acid, by the same procedure, Morton obtained 1.84 × 10^{-5}, which may be compared with 1.749 × 10^{-5} as determined by Harned and Ehlers.[3]

A number of objections may be raised to the methods employed for the determination of K_B. Zawidzki was not able, by addition of excess cacodylic acid, to repress the reaction

$$(CH_3)_2AsOOH \cdot H^+ + H_2O \longrightarrow (CH_3)_2AsOOH + H_3O^+$$

so as to obtain the mobility of the cation, and in his computation of the degree of hydrolysis he took $\Lambda_{HCac \cdot H^+} = \Lambda_{Cac^-}$. Johnston's value is an estimated one based on Zawidzki's Λ_{Cac^-}. Turning to Holmberg's kinetic determination, the four values of K_B show considerable variation (54, 42, 48, 60); this Holmberg believed due to the speed of the reaction, which made it necessary to work at low concentrations (*ca.* 0.001 *M*) of strong acid. It may also be mentioned that the decomposition of diazoacetic ester is known to have a very high positive primary kinetic salt effect, and that in the presence of many anions, among them nitrate, a side reaction occurs.

In this paper there are presented the results of another kinetic determination of K_B, the reaction employed being the hydrolysis of ethylene acetal, which Brönsted and Grove[4] showed to be catalyzed specifically by the hydrogen ion.

There are also presented some colorimetrically and some electrometrically determined values of K_A; the latter are due to Chase.[5]

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(1) (a) Zawidzki, *Ber.*, **36**, 3325 (1903); **37**, 2289 (1904); (b) Johnston, *ibid.*, **37**, 3625 (1904); (c) Holmberg, *Z. physik. Chem.*, **70**, 153 (1910).

(2) Morton, *J. Chem. Soc.*, 1401 (1928).

(3) Harned and Ehlers, THIS JOURNAL, **55**, 652 (1933); the constant has been converted from the molality to the molarity scale.

(4) Brönsted and Grove, *ibid.*, **52**, 1394 (1930).

(5) Present address of Dr. E. F. Chase, Drexel Institute of Technology, Philadelphia.

Experimental Part

Ethylene Acetal.—The ethylene acetal was prepared by L. C. Riesch according to the method of Brönsted and Grove. It boiled at 82.9–83.5°, at 769 mm., and tested free of acid.

Cacodylic Acid.—Kahlbaum cacodylic acid was dissolved in hot 95% ethanol, and on cooling was precipitated by addition of an equal volume of ethyl ether. Two recrystallizations were made. Upon removal from the desiccator the samples were dried in the oven at 110° to constant weight before use. The purity, as determined by electrometric titration against standard sodium hydroxide solution, in an atmosphere of nitrogen, was 100.04%. This lot of acid was used in the kinetic and colorimetric experiments.

γ-Dinitrophenol.—The 2,5-dinitrophenol was a La Motte preparation, m. p. 106.1–106.3°, cor.

The Kinetic Determination of K_B.—The rate of hydrolysis of ethylene acetal was measured by observing the contraction of the solution in a dilatometer previously used by Martin Kilpatrick,[6] and described by him. The results obtained are presented in Table I.

TABLE I

THE EFFECT OF CACODYLIC ACID UPON THE HYDROLYSIS OF ETHYLENE ACETAL AT CONSTANT HYDROCHLORIC ACID CONCENTRATION

$M_{\text{HCl}} = 0.03103$; $M_{\text{E. Acetal}} = 0.1$; T, 25.00°

Stoic. molarity HCac	$k_{\text{obs.}}$ in min.$^{-1}$	Moles per liter H_3O^+	Moles per liter $HCac \cdot H^+$	K_B
0.0	0.02487[a]	0.03103	0.0	0.0
.02010	.01759	.02195	.00908	37.5
.03015	.01497	.01867	.01236	37.2
.04031	.01283	.01600	.01503	37.2
.05044	.01112	.01388	.01715	37.1
.06049	.00970	.01209	.01894	37.7
.07052	.00866	.01080	.02023	37.2
				Av. 37.3

[a] Average of 4 expts.

The second column gives the first-order velocity constant calculated from the dilatometer readings by Guggenheim's method, the third column, the hydrogen-ion concentration taken as $k_{\text{obs.}}/(0.02487/0.03103)$, and the fourth column, the concentration of the cation taken as $0.03103 - [H_3O^+]$. It will be observed that the ionic strength remained constant throughout the series of experiments, and that no medium effect of the non-electrolyte was detected.

Since $K_B \neq 0$, and since $[(CH_3)_2AsOOH \cdot H^+]/[H_3O^+] = K_B[(CH_3)_2AsOOH]$, the ratio of the concentration of cation to that of the hydrogen ion drops off upon dilution of a solution of cacodylic acid, and if K_A is computed from the conductance in the manner used for a simple monobasic acid, it appears to increase with dilution. On the other hand, in the presence of bases much stronger than itself, *e. g.*, in the presence of cacodylate ion, the acid behaves like a simple monobasic acid; thus in a buffer solution 0.005 M in sodium cacodylate and 0.025 M in cacodylic acid the hydrogen-ion concentration is 0.1% smaller than would be the case were $K_B = 0$.

The Colorimetric Determination of K_A.—A value of the acid strength of cacodylic acid, relative to that of acetic, was obtained by determining colorimetrically the equilibrium constants K_{AiB_1} and K_{AiB_2} for the reactions (1) acetate + γ-dinitrophenol $\rightleftarrows$ acetic acid + γ-dinitrophenolate; (2) cacodylate + γ-dinitrophenol $\rightleftarrows$ cacodylic acid + γ-dinitrophenolate, from which it follows that $K_{\text{HCac}}/K_{\text{HAc}} = K_{\text{AiB}_1}/K_{\text{AiB}_2}$.

The determinations were made with an Evelyn photoelectric colorimeter manufactured by the Rubicon Co., Philadelphia. Measurements were made in duplicate in calibrated test-tubes, with no. 420 filter, which has negligible transmittance below 3800 and above 4600 Å. The extinctions of the indicator in the complete acid form (E_{Ai}) and in the complete basic form (E_{Bi}) were determined from measurements in 0.1 N hydrochloric acid and in 0.005 N sodium hydroxide solution, respectively. Thus, to obtain E_{Bi} a solution 5.07×10^{-5} M in γ-dinitrophenol and 0.005 N in sodium hydroxide was diluted with 0.005 N sodium hydroxide solution, and the extinction E_{Bi} was calculated from the galvanometer readings by means of the equation

$$\log G_0 - \log G = E_{\text{Bi}}F$$

where F is the fraction of the original amount of indicator, and G_0 the galvanometer reading for the blank, 0.005 N sodium hydroxide. The instrument was adjusted before each measurement to give a reading of 100.0 with the blank. The extinction E_{Bi} was taken as the slope of the line passing through $\log G_0$, as computed by the method of least squares; within the experimental error, $(\log G_0 - \log G)/F$ was constant. There are shown in Table II the results obtained upon diluting a 1:3 acetic acid–sodium acetate, and a 5:1 cacodylic acid–sodium cacodylate buffer solution from $\mu = 0.05$ to $\mu = 0.01$, the indicator ratio being calculated from the formula

$$[\text{Bi}]/[\text{Ai}] = \{E - E_{\text{Ai}}\}/\{E_{\text{Bi}} - E\}$$

TABLE II

THE STRENGTH OF CACODYLIC ACID RELATIVE TO ACETIC

$M_{\gamma\text{-Dnp}} = 5.07 \times 10^{-5}$; $E_{\text{Ai}} = 0.0380$[a]; $E_{\text{Bi}} = 0.3355$; T, 25°

Stoichiometric molarity Acetate HAc	Stoichiometric molarity Acetate NaAc	Stoichiometric molarity Cacodylate HCac	Stoichiometric molarity Cacodylate NaCac	$E = \log G_0 - \log G$ Acetate buffer	$E = \log G_0 - \log G$ Cacodylate buffer	$K_{\text{AiB}_1}/K_{\text{AiB}_2}$
0.01671	0.05006	0.2499	0.05004	0.1909	0.2443	0.0312
.01337	.04005	.1999	.04003	.1905	.2468	.0298
.01003	.03004	.1499	.03002	.1896	.2437	.0310
.006684	.02002	.09996	.02002	.1905	.2441	.0311
.003342	.01001	.04998	.01001	.1898	.2451	.0303
					Av.	0.0307
					a. d.	1.6%

[a] Measured at 22°.

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[6] Kilpatrick, THIS JOURNAL, 50, 2891 (1928).

Standard 0.1 N sodium hydroxide was used in preparing the buffer solutions.

A duplicate determination gave K_{AiB_1}/K_{AiB_2} = 0.0309, a.d. 0.6%. The average value is 0.0308, from which $(K_A)_0 = 5.39 \times 10^{-7}$ if the dissociation constant of acetic acid is taken[3] as 1.749×10^{-5}. This result is based upon the assumption of constancy of $E_{Ai}/[Ai]$ and $E_{Bi}/[Bi]$. It may be mentioned that increase in $E_{Ai}/[Ai]$ and $E_{Bi}/[Bi]$ with decrease in [Ai] and [Bi], respectively, would have very little effect upon the ratio K_{AiB_1}/K_{AiB_2}, although it would affect the individual equilibrium constants to a considerable extent. It may also be mentioned that K_{AiB_1} was found to be 0.350, K_{AiB_2} 11.4; the former figure may be compared with 0.347 found by Judson.[7] For the ratio of the acid dissociation constants Morton obtained $K_{HCac}/K_{HAc} = 5.66 \times 10^{-7}/1.84 \times 10^{-5} = 0.0308$, at 30°.

The Electrometric Determination of K_A in Potassium Chloride Solution

Buffer solutions were prepared from Kahlbaums best grade of cacodylic acid, sodium cacodylate and potassium chloride. The acid content was determined by titration of the stock solution of cacodylic acid with standard sodium hydroxide, and the cacodylate content by titration of the stock solution of sodium cacodylate with hydrochloric acid. By titration, the Kahlbaum salt was found to be 72.65% sodium cacodylate; upon heating for twenty-four hours in the oven at 120°, the loss in weight was 27.32%.

In the cell used there were two quinhydrone electrodes connected by a saturated potassium chloride bridge, and the ionic strength of the solution in each electrode compartment was μ (chiefly potassium chloride). See the article by Chase and Kilpatrick[8] for a description of the apparatus and procedure.

With the cacodylate buffers the potentials were constant and reproducible, and measurements on the same buffer solutions eight months later gave values of the hydrogen-ion concentration differing from the original by less than 1%. The results are summarized in Table III. Each value of K_A is the average for three experiments, in which the stoichiometric molarities of the buffer constituents were

M_{NaCac}	M_{HCac}
0.007265	0.01001
.007265	.02002
.01453	.01001

No trend appeared in K_A with change of buffer ratio. It should be pointed out that the buffer solutions were prepared on the supposition that the sodium cacodylate was anhydrous, and that in consequence the ionic strengths were a little lower than the nominal values, *e. g.*, at $\mu = 0.5$ the buffer solutions were of ionic strength 0.497, 0.497 and 0.495, respectively, $\mu_{Av.} = 0.496$. The K_A's given in the third and sixth columns are smoothed values read off from a plot of $\{\log K_A - \sqrt{\mu}\}$ *vs.* μ at round concentrations, 0.100, 0.300, etc.

Table III

The Classical Dissociation Constant of Cacodylic Acid in Potassium Chloride Solution at 25°

Data of Chase

μ	$K_A \times 10^7$ Exptl.	Calcd.	μ	$K_A \times 10^7$ Exptl.	Calcd.
0.1	8.49 ± 0.04	8.41	1.5	6.87 ± 0.03	6.86
.3	8.95 ± .08	8.97	2.0	5.56 ± .02	5.56
.5	9.09 ± .03	9.08	2.5	4.49 ± .02	4.45
.7	8.75 ± .05	8.79	3.0	3.54 ± .03	3.54
1.0	8.09 ± .07	8.05			

From the K_A's of Table III, in conjunction with the corresponding values of the dissociation constant of acetic acid in potassium chloride solution, an estimate of K_A at infinite dilution may be made by means of the equation

$$\log (K_{HCac}/K_{HAc}) = \log (K_{HCac}/K_{HAc})_0 + \beta\mu$$

where β, which may be positive or negative, is a constant for a given solvent salt. The top curve of Fig. 1 shows the results obtained upon taking for the dissociation constant of acetic acid the values determined by Kilpatrick, Chase and Riesch[9] with the same apparatus used in the present investigation, and the curve next to the top shows the results obtained upon taking the values of Harned and Hickey,[10] converted to the molarity scale. The two lower curves, which show Mor-

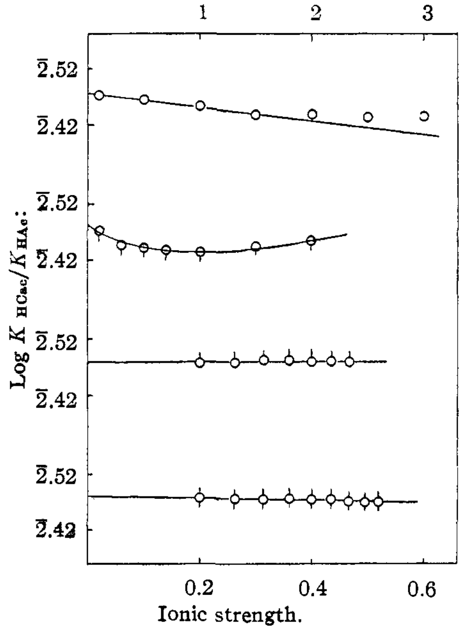

Fig. 1.—Log K_{HCac}/K_{HAc} as a function of ionic strength: ○ and ♀ KCl solution, scale at top. ȯ NaCl solution; ȯ BaCl$_2$ solution, scale at bottom; data of Morton.

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[7] C. M. Judson, Dissertation, University of Pennsylvania, 1947.

[8] Chase and Kilpatrick, This Journal, **53**, 2859 (1931).

[9] Kilpatrick, Chase and Riesch, *ibid*, **56**, 2051 (1934).

[10] Harned and Hickey, *ibid.*, **59**, 2303 (1937).

ton's results, were constructed as follows. The values of the dissociation constant of acetic acid were corrected for the ionization of the acid, {log $K_{HAc} - \sqrt{\mu}$} was plotted *vs.* μ, and values of K_{HAc} were read off from the curve at those ionic strengths at which K_{HCac} was measured. The curves of Fig. 1 show log (K_{HCac}/K_{HAc}) thus found for the soutions[11] where M_{NaCac} (and $M_{NaAc}) \leqq \mu/5$.

Application of the method of least squares to the data of Chase for cacodylic acid (smoothed values, $\mu < 2.0$), and the data of Kilpatrick, Chase and Riesch for acetic acid, gave

$$\log (K_{HCac/HAc}) = \bar{2}.476 - 0.024\mu \text{ in KCl soln.}$$

The curve obtained using the data of Harned and Hickey for acetic acid is not linear; as drawn, the intercept is $\bar{2}.482$. Application of the method of least squares to Morton's data gave

$$\log (K_{HCac}/K_{HAc}) = \bar{2}.479 + 0.005\mu \text{ in NaCl soln.}$$

$$\log (H_{HCac}/K_{HAc}) = \bar{2}.481 - 0.012\mu \text{ in BaCl}_2 \text{ soln.}$$

These intercepts may be compared with log 0.0308 = $\bar{2}.489$ determined colorimetrically. The average of the electrometric and colorimetric results at 25° is $\bar{2}.484$ which is probably correct to 0.01; the dissociation constant of cacodylic acid computed from this figure is 5.33×10^{-7}.

Figure 1 and Tables II and III show that the change of K_A with μ closely parallels that for acetic acid, which indicates that cacodylic acid is present in aqueous solution as neutral molecule, rather than as zwitterion.

Acknowledgment.—The writer wishes to thank Dr. E. F. Chase for kindly permitting the publication of Table III. She also wishes to thank Dr. L. C. Riesch for preparing the ethylene acetal.

Summary

At 25°, the basic strength of cacodylic acid was found by a kinetic method to be 37.3 at $\mu = 0.03$, and the acid strength, which was determined both colorimetrically and (by Chase) electrometrically, to be $5.33 \pm 0.10 \times 10^{-7}$ at $\mu = 0$. The figure for the acid strength is in satisfactory agreement with the results of Morton.

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[11] Morton's data in potassium and magnesium sulfate solution are not included because of involvement of the sulfate-bisulfate equilibrium.

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Rate Constants in Free Radical Polymerizations. II. Vinyl Acetate[1]

BY M. S. MATHESON, E. E. AUER, ELLEN B. BEVILACQUA[2] AND E. J. HART[3]

The absolute rate constants of vinyl acetate polymerization have previously been measured both by Burnett and Melville[4] and by Swain and Bartlett[5] through the use of the rotating sector technique, but the results are in disagreement. More recently the viscosity method of Bamford and Dewar has been applied to vinyl acetate[6] with results in fair agreement with those of Swain and Bartlett.

In the first paper of this series the application of the rotating sector to the measurement of the rate constants in methyl methacrylate[7] polymerization was described. We have now applied the method to vinyl acetate in an attempt to resolve the discrepancy in the literature, and this paper reports and discusses the results obtained.

Experimental

Vinyl Acetate.—Nozaki and Bartlett[8] have shown how difficult is the purification of vinyl acetate. In the present work, the preparation of pure vinyl acetate free of inhibiting impurities was found to be the major experimental problem encountered in the studies on this monomer. In the procedure finally adopted, 4 liters of commercial vinyl acetate (Eastman Kodak Co.) was distilled under purified nitrogen through a 60-plate glass column packed with glass helices. The automatic takeoff was set at 5% and the middle 2-liter fraction collected (b. p. 73.1° at 761 mm., uncor. $n^{20}\text{D}$ 1.3959) in one-liter round bottom flasks, 500 cc. to a flask. In ref. 8 b. p. 72.4° (760 mm.) and $n^{25}\text{D}$ 1.3934 reported.

Figure 1 shows a receiver flask F. During distillation F was attached to the distillation head by the joint J_1-J_1'. When a suitable fraction was received in F, the flask was removed and attached to a vacuum system by means of joint J_1 with D stoppered. The flask was degassed quickly and flushed with purified nitrogen, D being sealed off at B. Finally the flask, at −78°, was filled with purified dry nitrogen to 1 atm. and sealed off at A. The flasks were stored at −25° in the dark until used. For use the flask was opened by breaking the tubing at C and was then attached promptly by male joint J_2 to the vacuum system at J_2'. The vinyl acetate was then thoroughly degassed (to $< 10^{-4}$ mm. permanent gas pressure), stopcock S was closed and the evacuated flask and attached stopcock were removed from the vacuum system by breaking the tube at E. Next the evacuated flask was irradiated in a water-bath at 30°, with an Hanovia Type A quartz arc about 3 inches away. After polymerization was estimated to be

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[1] In this paper a few of the final experiments and all of the preparation for publication were carried out with the assistance of the Office of Naval Research under Contract N8 onr-544.

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[4] (a) G. M. Burnett and H. W. Melville, *Nature*, **156**, 661 (1945); (b) *Proc. Roy. Soc.* (*London*), **A189**, 456 (1947).

[5] (a) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **67**, 2273 (1945); (b) C. G. Swain and P. D. Bartlett, *ibid.*, **68**, 2381 (1946).

[6] C. H. Bamford, The Labile Molecule, *Discussions of the Faraday Soc.*, No. 2, 317 (1947); G. Dixon-Lewis, *ibid.*, 319.

[7] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

[8] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 2377 (1946).