

been made on cells  $H_2(1 \text{ atm.}), HCl(m \text{ in } 10 \text{ and } 20\% C_2H_5OH - H_2O), AgCl(s) + Ag(s)$ .

2. Vapor pressure and density measurements of the solvent have been made and tabulated

for the temperature range 0 through 40°.

3. The molal electrode potentials of the silver-silver chloride electrode have been calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

## The Ionization Constants of Propionic Acid in Methyl and Ethyl Alcohol-Water Mixtures from 0 Through 40°<sup>1</sup>

BY ANDREW PATTERSON<sup>2</sup> WITH W. A. FELSING

The purpose of this investigation was the determination of the ionization constants of a weak acid in solvent media of lower dielectric strength than that of water. Harned and Embree<sup>3</sup> have shown that the electromotive forces of cells of the type  $H_2(1 \text{ atm.}), (HA(m_1), NaA(m_2), NaCl(m_3)) \text{ in}$

$x \text{ alcohol-water}, AgCl(s) + Ag(s)$

may be used to calculate the ionization constants of weak acids in water-alcohol mixtures, provided the dielectric strength does not become low enough to permit ionic association.

For this study, propionic acid in solution with 10 and 20% methyl and ethyl alcohol-water mixtures was chosen; measurements were proposed at 0, 10, 20, 25, 30, and 40°.

### Materials Used

**Propionic Acid.**—C. P. Eastman Kodak Co. propionic acid was separated into fractions by distillation through a two-meter column packed with berl saddles, the first and last portions being discarded. The middle portions selected for use had a refractive index  $n^{20D} 1.3874$  (literature<sup>4</sup> value,  $n^{19.9D} 1.38736$ ), and an analysis confirmed their purity. **Sodium Propionate.**—This salt was prepared from purified propionic acid and sodium carbonate by the method of Watson and Felsing<sup>5</sup>; analysis of the product indicated high purity. **Sodium Chloride.**—Reagent grade material was precipitated thrice with hydrogen chloride, washed with cold distilled water, and centrifuged. **Methyl Alcohol.**—A high grade stock material was fractionated three times through a one-meter packed column, the first and last portions being discarded each time. The final fractionation yielded material having a refractive index  $n^{20D} 1.3288$  (literature<sup>6</sup> value,  $n^{20D} 1.329$ ). **Ethyl Alcohol.**—The preparation of this alcohol was described in a previous paper.<sup>7</sup>

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(3) Harned and Embree, *THIS JOURNAL*, **57**, 1669 (1935).

(4) "International Critical Tables," Vol. 7, p. 35.

(5) Watson with Felsing, *THIS JOURNAL*, **63**, 410 (1941).

(6) "International Critical Tables," Vol. 7, p. 79.

(7) Patterson with Felsing, *THIS JOURNAL*, **64**, 1478 (1942).

**Solutions.**—Concentrated stock solutions were prepared by choosing the relative amounts of dry alcohol, water, propionic acid, sodium propionate, and sodium chloride to yield a solution which was approximately molal in each of the three solutes, while the solvent consisted of either 10 or 20% of methyl or ethyl alcohol in water. All solutions were made by weight. From these stock solutions, the cell solutions were prepared by dilution. All solutions were kept from contact with air as nearly as possible; hydrogen was bubbled through all solutions immediately prior to their introduction into the cells. The concentrations  $m_1$ ,  $m_2$ , and  $m_3$  were known to an accuracy of 0.1%; the cell solutions were introduced by a vacuum technique to avoid contact with air. The total vapor pressures of all solutions were determined experimentally.<sup>7</sup>

**Experimental Results.**—Each recorded electromotive force in Tables I and II is the average of three separate cell values at each temperature except at 25°, where six measurements were made. The temperature range was covered by two sets of cells containing solution of the same concentration: one from 0 through 25° and the other from 25 through 40°. All electromotive forces were corrected to a partial pressure of one atmosphere of hydrogen; the observed voltage of one cell remained constant within  $\pm 0.05$  mv. after attaining equilibrium, and the voltages of a set of cells were reproducible to within 0.2 mv.

**Ionization Constant.**—The equation for the electromotive force of the cells measured may be written

$$\left( E_{\text{obs.}} - E_0' - \frac{RT}{F} \ln \frac{m_{\text{HPr}} m_{\text{Cl}^-}}{m_{\text{Pr}^-}} \right) = \left( - \frac{RT}{F} \ln \frac{\gamma_{\text{H}^+} \gamma_{\text{Cl}^-} \gamma_{\text{HPr}}}{\gamma_{\text{H}} \gamma_{\text{Pr}^-}} - \frac{RT}{F} \ln K_{\text{HPr}} \right)$$

where  $E_0'$  is the molal electrode potential of the silver-silver chloride electrode in the particular solvent medium,  $K$  is the ionization constant of the acid and  $\gamma$  and  $m$  are the respective activity coefficients and molalities. By inspection it is seen that  $m_{\text{HPr}} = (m_1 - m_{\text{H}})$  and  $m_{\text{Pr}^-} = (m_2 - m_{\text{H}})$ ; however, these quantities may be replaced with  $m_1$  and  $m_2$ , since propionic

TABLE I  
ELECTROMOTIVE FORCES OF CELLS  $H_2$  (1 ATM.),  $(HPr(m_1), NaPr(m_2), NaCl(m_3)$  in  $x$  METHYL ALCOHOL-WATER),  $AgCl(s) + Ag(s)$

$m_1$	0°	$m_2 = 1.1382m_1, x = 10\%, m_3 = 1.0973m_1$			30°	40°
		10°	20°	25°		
0.07872	0.56474	0.57151	0.57798	0.58127	0.58486	0.59137
.06565	.56905	.57568	.58252	.58584	.58956	.59615
.06331	.56985	.57651	.58358	.58672	.59048	.59699
.05367	.57340	.58048	.58757	.59095	.59470	.59948
.04486	.57792	.58480	.59205	.59550	.59929	.60623
.03439	.58399	.59090	.59856	.60204	.60664	.61325
.02765	.58760	.59614	.60401	.60751	.61148	.61912
.02054	.59463	.60315	.61139	.61455	.61899	.62708
.01213	.60695	.61558	.62458	.62803	.63261	.64112
.00897	.61377	.62272	.63169	.63574	.64007	.64921
		$m_2 = 1.1549m_1, x = 20\%, m_3 = 1.1001m_1$				
0.06729	0.57201	0.57924	0.58738	0.59082	0.59459	0.60185
.06045	.57514	.58186	.58978	.59351	.59740	.60461
.05369	.57797	.58466	.59259	.59652	.60040	.60781
.04859	.57998	.58709	.59497	.59907	.60292	.61051
.03736	.58615	.59346	.60146	.60576	.60981	.61751
.03117	.59045	.59783	.60599	.61005	.61449	.62240
.02283	.59697	.60543	.61384	.61798	.62251	.63077
.01726	.60206	.61101	.62089	.62514	.62974	.63821
.01110	.61237	.62264	.63195	.63634	.64120	.65001
.00607	.62549	.63594	.64686	.65158	.65669	.66623

TABLE II  
ELECTROMOTIVE FORCES OF CELLS  $H_2$  (1 ATM.),  $(HPr(m_1), NaPr(m_2), NaCl(m_3)$  in  $x$  ETHYL ALCOHOL-WATER),  $AgCl(s) + Ag(s)$

$m_1$	0°	$m_2 = 1.1036m_1, x = 10\%, m_3 = 1.1302m_1$			30°	40°
		10°	20°	25°		
0.07825	0.56232	0.57045	0.57711	0.58031	0.58467	0.59074
.06944	.56514	.57329	.57903	.58334	.58763	.59384
.06034	.56809	.57661	.58354	.58688	.59099	.59758
.04928	.57271	.58403	.58875	.58995	.59601	.60281
.04048	.57727	.58617	.59331	.59687	.60087	.60811
.03540	.58035	.58932	.59657	.60030	.60415	.61162
.02420	.58910	.59848	.60602	.60993	.61407	.62184
.01789	.59607	.60566	.61354	.61763	.62191	.62993
.00392	.61373	.62377	.63270	.63584	.64182	.64982
		$m_2 = 1.0793m_1, x = 20\%, m_3 = 1.0782m_1$				
0.07701	0.56546	0.57355	0.58088	0.58608	0.58946	0.59691
.06635	.56872	.57719	.58464	.58865	.59332	.60084
.05697	.57220	.58081	.58814	.59240	.59708	.60431
.05070	.57479	.58356	.59081	.59533	.59982	.60747
.04022	.58006	.58919	.59659	.60114	.60546	.61349
.03375	.58410	.59341	.60088	.60561	.60675	.61796
.02569	.58996	.59919	.60735	.61200	.61672	.62467
.01926	.59312	.60498	.61363	.61891	.62366	.63028
.01178	.60423	.61587	.62463	.62975	.63477	.64312
.00638	.61731	.62720	.63692	.64208	.64729	.65616

acid is a weak acid and is in the presence of one of its highly active salts. To evaluate  $K$ , the left side of the equation was allowed to become  $(-\log K')$  in which  $K'$  is a spurious value of the ionization constant and evaluated from the known value of  $E_0'$ , the observed  $E$ 's, and the calculated molalities. The values of  $(-\log K')$  were plotted

as a function of the ionic strength; the extrapolation to zero ionic strength, where all the activity coefficients involved became unity, yielded a value of  $K'$  which was equal to that of  $K$ .

Table III presents the values of  $K$  obtained in the various solvent media at the different temperatures employed.

TABLE III  
VALUES OF  $K$  IN 10 AND 20 PER CENT. METHYL AND ETHYL  
ALCOHOL SOLUTIONS

Methyl Alcohol Solutions							
°C.....	0	10	20	25	30	40	
10%	0.8812	0.8853	0.9173	0.9471	0.9093	0.8379	
20%	.6026	.6082	.5860	.5776	.5528	.5254	
Ethyl Alcohol Solutions							
10%	0.8625	0.8700	0.9000	0.9004	0.9061	0.9020	
20%	.6730	.7546	.7706	.7811	.7880	.7803	

The curvature of the lines in the plots relating ( $-\log K'$ ) to ionic strength was more pronounced in this investigation than in investigations using acids of smaller molecular size and media of higher dielectric strength. In solutions of lower dielectric

strength (as the 20% ethyl alcohol solutions) the curvature was sufficiently great to make accurate extrapolation difficult. This effect was greatest at higher temperatures.

### Summary

1. Electromotive force measurements have been made on cells of the type  $H_2(1 \text{ atm.}), (HPr(m_1), NaPr(m_2), NaCl(m_3))$  in  $x$  alcohol-water,  $AgCl(s) + Ag(s)$ , where  $x$  is the per cent., either 10 or 20, of methyl or ethyl alcohol.

2. Values of the ionization constants of the propionic acid in 10 and 20% alcohol-water solutions have been determined over the temperature range 0 through 40°.

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## NOTES

### Synthesis of 4,4'-Dicyanostilbene

BY SHOU-CHENG FU<sup>1</sup> AND PETER P. T. SAH<sup>2</sup>

4,4'-Dicyanostilbene, a valuable intermediate which has been used in the synthesis of the pharmacologically<sup>3</sup> interesting 4,4'-diamidinostilbene, has been prepared from *p*-cyanobenzaldehyde through the pyrolysis of the corresponding azine.

**4,4'-Dicyanobenzaldazine.**—*p*-Cyanobenzaldehyde<sup>4</sup> (4 g.) and hydrazine hydrate (40%, 1.5 g.) in 30 cc. of absolute ethanol were heated four hours under reflux. The reaction mixture was concentrated to ca. 5 cc.; the pale yellow needles which separated on cooling were collected and recrystallized twice from dilute ethanol, yellow needles (2.5 g.); m. p. 118–120° (uncor.).

*Anal.* Calcd. for  $C_{16}H_{10}N_4$ : N, 21.70. Found: N, 21.60.

**4,4'-Dicyanostilbene.**—4,4'-Dicyanobenzaldazine (2 g.), on heating first melted, then decomposed, then sublimed as beautiful long needles and narrow plates. Repeated sublimation gave 500 mg. of practically colorless 4,4'-dicyanostilbene, m. p. 278–280° (cor.), mixed with a sample prepared by the method of Lamb and White,<sup>5</sup> but purified by sublimation; m. p. 278–280° (cor.).

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(2) The authors wish to thank Dr. Hamilton H. Anderson, Professor of Pharmacology and Chairman of the Department, Peiping Union Medical College, for his kindness in suggesting this problem.

(3) Yorke, *Transactions of the Royal Society of Tropical Medicine and Hygiene*, **33**, 464 (1940).

(4) Moses, *Ber.*, **33**, 2624 (1900).

(5) Lamb and White, *J. Chem. Soc.*, 1253 (1939).

### Rotational Relationships of Alkyl Glucosides

BY LEONARD C. KREIDER AND ELMER FRIESEN<sup>1</sup>

The problem of finding simple relationships between the structures of glycosides and glycoside acetates and their optical rotations first attracted our attention when we noticed that the earlier theories proposed by Hudson<sup>2</sup> and Maltby,<sup>3</sup> stating that molecular rotations of glucosides increased in magnitude with increasing molecular weight, were inconsistent with the data more recently obtained on the higher homologs of the alkyl glucosides. In the effort to develop a consistent theory that suggested itself to us,<sup>4</sup> we have prepared a number of new glucoside acetates, following the method of Kreider and Evans,<sup>5</sup> and from these we have prepared the glucosides, following the method of Isbell,<sup>6</sup> and have measured the rotations and other properties of these substances. The resulting data are contained in Table I.

In addition, we have measured the rotations in chloroform of the following substances kindly supplied to us by Noller and Rockwell<sup>7</sup> for this

(1) Present address: Redman Scientific Company, Los Angeles, California.

(2) C. S. Hudson, *THIS JOURNAL*, **31**, 66 (1909).

(3) J. C. Maltby, *J. Chem. Soc.*, **123**, 1404 (1923).

(4) Preliminary report, Meeting of the Kansas Academy of Science, April 4, 1941.

(5) L. C. Kreider and W. L. Evans, *THIS JOURNAL*, **58**, 797, 1661 (1936).

(6) H. S. Isbell, *Bur. Standards J. Research*, **5**, 1179 (1930).

(7) C. R. Noller and C. W. Rockwell, *THIS JOURNAL*, **60**, 2076 (1938).