49. *Precise Measurements, with the Glass Electrode, of the Ionization Constants of Benzoic, Phenylacetic, and β-Phenylpropionic Acids at 25°.*

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The ionization constants of three aromatic acids have been obtained from measurements on cells containing silver–silver chloride electrodes and glass electrodes of low resistance. The change in electromotive force was determined at the moment of transfer of the glass electrode between a cell containing a buffer solution of acetic acid and one containing a buffer solution of the weak acid under study. This comparison eliminates the effect of asymmetry potential. The behaviour of the glass electrode is more reproducible and accurate in transfers between buffer solutions of similar pH values than it is between hydrochloric acid and a buffer solution of a weak acid. At 25° the thermodynamic p*K* values for benzoic, phenylacetic, and β-phenylpropionic (dihydrocinnamic) acid are, respectively, 4·2050 ± 0·0015, 4·3074 ± 0·0010, and 4·6644 ± $0{\cdot}0005_5$. The precision of these measurements is thus as good as that obtainable with a hydrogen electrode.

ONE of the most convenient and precise methods of determining ionization constants of weak acids makes use of cells, without liquid junction, containing hydrogen and silver chloride electrodes. Because aromatic and unsaturated acids are reduced at the hydrogen electrode, the method is usually restricted to saturated aliphatic acids. There are, moreover, many inorganic acids that, because of their oxidizing action, cannot be studied with a hydrogen electrode. Recently it has been shown [1] that glass electrodes of low resistance give results with strong acids that are as precise as those obtained with the hydrogen electrode. We have now tested the performance of these glass electrodes in weak acid

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[1] Covington and Prue, *J.*, 1955, 3696.

buffers and have obtained ionization constants of three aromatic acids with a precision of better than 0·1 mv in electromotive force or 0·002 in pK.

In the earlier work on strong acids the change in electromotive force (ΔE) was determined for transfer of the glass electrode between solutions of the acid of different concentration. Because of the drift in asymmetry potential with time, it was necessary by a simple extrapolation to determine ΔE at the instant of transfer. We first attempted to apply this procedure to transfers of the glass electrode between the cells

$$\boxed{\text{Ag|AgCl|HCl(0·12m)}}\ \text{glass|HCl(0·01m)|AgCl|Ag}$$

and

$$\boxed{\text{Ag|AgCl|HCl(0·12m)}}\ \text{glass|HX(m), NaX(m), NaCl(m)|AgCl|Ag}$$

where HX represents the weak acid under study. The enclosed part on the left of the cells represents the glass electrode filled with hydrochloric acid and containing an internal silver–silver chloride reference electrode. Because the activity of 0·01m-hydrochloric acid is well established,[2] these measurements would give the ionization constant of the weak acid. It was unfortunately impossible to obtain results of satisfactory precision with our glass electrodes, for they frequently did not give the theoretical response when transfer was made between two solutions of widely different pH values, though it is possible that other carefully selected and protected glass electrodes may perform satisfactorily in such transfers.[3] In general one must expect considerable individuality in behaviour of glass electrodes, especially when a precision of better than 0·1 mv is required.

Satisfactory results were obtained by making transfers of the glass electrode between solutions that had similar pH values. We have used an acetate buffer as the reference solution in place of 0·01m-hydrochloric acid. Electromotive forces, E_s and E_x, were determined at the instant of transfer between cells S and X:

Glass electrode|HOAc(0·01m), NaOAc(0·01m), NaCl(0·01m)|AgCl|Ag . (S)
Glass electrode|HX(m), NaX(m), NaCl(m)|AgCl|Ag . . . . (X)

It was assumed that the asymmetry potential of the glass electrode makes the same contribution to E_s and to E_x and is eliminated in taking the difference. Then we have:

$$\Delta E = E_s - E_x = -\frac{(\ln 10)\boldsymbol{R}T}{\boldsymbol{F}}\log\frac{\mathrm{m'_H}\gamma'_{\mathrm{H}}\mathrm{m'_{Cl}}\gamma'_{\mathrm{Cl}}}{\mathrm{m_H}\gamma_{\mathrm{H}}\mathrm{m_{Cl}}\gamma_{\mathrm{Cl}}} \quad . \ . \ . \ . \quad (1)$$

where m′ and γ' are the molalities and activity coefficients in the standard buffer and m and γ are those in the buffer of cell X. If the hydrogen-ion activities are now eliminated by using the ionization constants of the acids, we obtain:

$$\frac{\boldsymbol{F}\Delta E}{(\ln 10)\boldsymbol{R}T} = \mathrm{p}K_{\mathrm{HOAc}} - \mathrm{p}K_{\mathrm{HX}} - \log\frac{\mathrm{m'_{Cl}}}{\mathrm{m_{Cl}}} - \log\frac{r'}{r} - \log\frac{\gamma'_{\mathrm{Cl}}\gamma'_{\mathrm{HOAc}}\gamma_{\mathrm{X}}}{\gamma_{\mathrm{Cl}}\gamma'_{\mathrm{OAc}}\gamma_{\mathrm{HX}}} \quad . \quad (2)$$

The buffer ratios are:

$$r' = \mathrm{m'_{HOAc}}/\mathrm{m'_{OAc}} = (0{\cdot}01 - \mathrm{m'_H})/(0{\cdot}01 + \mathrm{m'_H}) \quad . \ . \ . \ . \quad (3)$$

and

$$r = \mathrm{m_{HX}}/\mathrm{m_X} = (\mathrm{m} - \mathrm{m_H})/(\mathrm{m} + \mathrm{m_H}) \quad . \ . \ . \ . \ . \ . \ . \quad (4)$$

The hydrogen-ion molalities are small and are given with sufficient precision by $\mathrm{m'_H} = K_{\mathrm{HOAc}}$ and $\mathrm{m_H} = K_{\mathrm{HX}}$. We assume that the last term on the right of equation 2 is a linear function of the ionic strengths I' and I, and we can then write:

$$\log\frac{\gamma'_{\mathrm{Cl}}\gamma'_{\mathrm{HOAc}}\gamma_{\mathrm{X}}}{\gamma_{\mathrm{Cl}}\gamma'_{\mathrm{OAc}}\gamma_{\mathrm{HX}}} = B'I' - BI \quad . \ . \ . \ . \ . \ . \ . \quad (5)$$

where B and B' are specific reaction constants.

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[2] Bates, Guggenheim, Harned, Ives, Janz, Monk, Robinson, Stokes, Wynne-Jones, and Prue, *J. Chem. Phys.*, 1956, **25**, 361.

[3] Covington, personal communication.

For acetic acid we take $\mathrm{p}K = 4{\cdot}7567$ and $B' = -0{\cdot}061$.[4] We[5] have used $(\ln 10)\boldsymbol{RT}/\boldsymbol{F} = 59{\cdot}159$ mv. The equation for the calculation of the ionization constant of the acid HX relative to that of acetic acid at 25° then becomes:

$$\mathrm{p}K_{\mathrm{HX}} = 6{\cdot}759_4 - 0{\cdot}016904(\Delta E) + \log\,[\mathrm{m}(\mathrm{m} - \mathrm{m_H})/(\mathrm{m} + \mathrm{m_H})] + BI \quad . \quad (6)$$

where ΔE is in mv. Because B was unknown, measurements were made on buffer solutions of six or seven different ionic strengths in cell X. The extrapolation function

$$Y = \mathrm{p}K_{\mathrm{HX}} - BI \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

was calculated directly from the experimental data, and $\mathrm{p}K_{\mathrm{HX}}$ was found as the intercept at zero ionic strength.

EXPERIMENTAL

Materials.—Constant-boiling hydrochloric acid was chlorinated and boiled to eliminate bromide and iodide. A constant-boiling fraction, prepared by re-distillation, was diluted with conductivity water to give solutions of suitable strength. Sodium hydroxide was freed from carbonate by filtering a 50% solution of the " AnalaR " pellets. A stock solution was made by diluting the filtrate with conductivity water and was stored in a Polythene bottle equipped with a Pyrex siphon and protected with a soda-lime tube. No turbidity was obtained when this stock solution was mixed with 0·5N-barium chloride. The sodium hydroxide solution was initially standardized by weight-titration against standard hydrochloric acid and potassium hydrogen phthalate (National Bureau of Standards Sample 84f). The standardization against phthalate was rechecked three times. Sodium chloride of A.C.S. Reagent grade was purified and fused according to the directions of Pinching and Bates.[6] It contained less than 0·001% of bromide and 0·002% of sodium hydroxide. Silver oxide was precipitated by mixing very dilute solutions of silver nitrate and sodium hydroxide and was washed by decantation with water for a week. Conductivity water was prepared by passing distilled water through a column of mixed ion-exchange resins.

The benzoic acid was National Bureau of Standards Sample 39g., 99·99% pure. The phenylacetic and β-phenylpropionic (dihydrocinnamic) acid were products of the H.M. Chemical Company, Santa Monica, California. Both contained less than 0·004% of chloride, iron, phosphate, and heavy metals. Their purity was assayed by titration with standard sodium hydroxide solution. The phenylacetic acid was 99·98% pure; the other acid was 99·89% pure. " AnalaR " glacial acetic acid was fractionally frozen three times, one-third being discarded each time. A dilute solution was prepared and standardized against the sodium hydroxide solution.

Buffer solutions were prepared from weighed quantities of acid, sodium hydroxide, sodium chloride, and conductivity water. Buoyancy corrections were applied. It was convenient to prepare the standard acetate buffer of cell S by dilution of a more concentrated stock buffer. At least two different stock buffers were used in the determination of each ionization constant.

Electrodes.—These were similar to those used in previous work.[1] The glass electrodes were left for several weeks in 0·1M-hydrochloric acid and then were kept in either acetate or benzoate buffer. The electrodes were usually filled with 0·12m-hydrochloric acid; a few were used that contained the standard acetate buffer.

Apparatus.—The shielded leads were Telcon Type PT.1.GM.(Mod) non-microphonic cable (Telegraph Construction and Maintenance Co. Ltd., Mercury House, Theobalds Road, London, W.C.1.). The apparatus was otherwise virtually the same as that used previously. The temperature of the water thermostat was maintained at 25·00° ± 0·02°.

Experimental Procedure.—This too was similar to that in previous work. A glass electrode was brought to temperature equilibrium in a jar of acetate buffer in the thermostat. Then it was transferred successively to cell S, cell X, cell S, and cell X, being kept for 10 min. in each cell. Electrodes that gave useful results fell into two classes. The best electrodes usually showed a drift in potential of less than 0·05 mv during 10 min. in a given buffer. Their

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[4] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350; Guggenheim and Prue, " Physicochemical Calculations," 2nd edn., North-Holland Publ. Co., Amsterdam, 1956, pp. 338—339.

[5] Cf. Birge, *Reports Progr. Phys.*, 1941, **8**, 90.

[6] Pinching and Bates, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 311.

potential during the second immersion in a given buffer was within a few hundredths of a millivolt of its value during the first immersion. But the potential did show a gradual drift of several tenths of a millivolt from day to day. For these electrodes of the first class, ΔE was determined as in previous work by extrapolation to the moment of transfer.

Other electrodes showed a less steady response to transfers. The potential of one was steady for several minutes after transfer, then decreased. Others behaved in the opposite way; their potentials increased rapidly at first, then drifted gradually upwards. These changes were too great to permit concordant values of ΔE to be obtained by the extrapolation procedure. They were, however, sufficiently uniform from one buffer to the next to give steady values of ΔE at equal times after transfer in the two buffers. The average of these minute-by-minute values of ΔE agreed well with those obtained from the first class of electrode. When the minute-by-minute differences showed a marked trend or differed widely from one transfer to the next, the electrode was discarded. The instantaneous response to transfers of electrodes of the second class is apparently correct, and as long as deviations from this initial value occur uniformly from one buffer to another, such electrodes give accurate results.

RESULTS AND DISCUSSION

The molalities m for cell X and the changes in electromotive force with transfer ΔE are given in Table 1. With three exceptions the ΔE values are the average of the results from four glass electrodes or twelve transfers in all. For two buffers, only two glass electrodes were used; and for one buffer, only three. The average deviations of these mean values are given in the Table. The extrapolation functions Y, calculated from the data by means of equations 6 and 7, are also presented in Table 1. One result for β-phenylpropionic acid was discarded because it deviated widely from the rest, doubtless owing to some error in preparation of the solutions.

TABLE 1

m (mole kg.$^{-1}$)	ΔE (mv)	Y
	Benzoic acid	
0·005000	14·25 ± 0·07	4·2067
0·007426	24·30 ± 0·09	4·2121
0·01000	32·07 ± 0·06	4·2120
0·01236	37·55 ± 0·08	4·2125
0·01500	42·40 ± 0·11	4·2150
0·02000	49·66 ± 0·11	4·2183
	β-Phenylpropionic acid	
0·005000	−12·64 ± 0·06	4·6677
0·007500	−2·18 ± 0·02	4·6688
0·01000	+5·17 ± 0·02	4·6696
0·01200	9·85 ± 0·02	4·6705
0·01500	15·46 ± 0·03	4·6728
0·02000	22·67 ± 0·03	4·6761

m (mole kg.$^{-1}$)	ΔE (mv)	Y
	Phenylacetic acid	
0·009000	23·44 ± 0·01	4·3126
0·01000	26·16 ± 0·03	4·3131
0·01249	31·96 ± 0·03	4·3125
0·01500	36·50 ± 0·03	4·3156
0·01890	42·98 ± 0·03	4·3159
0·02500	49·49 ± 0·02	4·3191
0·03000	53·92 ± 0·02	4·3237

The values of pK and B in equation 7 were determined by the method of least squares. They are given in Table 2 together with their standard deviations, an indication of the reliability of the extrapolations. This Table also includes value of pK determined by other workers. All values of pK are for concentrations in moles per kg. of water.

Benzoic acid has been thoroughly investigated by several different methods and was used as a test of our technique. Our result was in good agreement with those of other workers. For β-phenylpropionic acid our result and the value from conductance measurements agree within the experimental errors. The agreement for phenylacetic acid is less good.

The B coefficients listed in Table 2 are all considerably larger than that of acetic acid (0·061 kg. mole^{-1}).

TABLE 2.

Acid	pK (This paper)	$-B$ (kg. mole^{-1})	pK (ref. *)
Benzoic	4·2050 ± 0·0015	0·335 ± 0·057	4·201 (*a*), 4·202 (*b*), 4·201 (*c*), 4·204 (*d*), 4·209 (*e*)
Phenylacetic	4·3074 ± 0·0010	0·253 ± 0·027	4·313 (*f*), 4·312 (*g*)
β-Phenylpropionic	4·6644 ± 0·0005$_5$	0·282 ± 0·022	4·661 (*h*)

* In parentheses.

Refs.: (*a*) Brockman and Kilpatrick, *J. Amer. Chem. Soc.*, 1934, **56**, 1483. (*b*) Saxton and Meier, *ibid.*, p. 1918. (*c*) Jones and Parton, *Trans. Faraday Soc.*, 1952, **48**, 8. (*d*) Robinson and Biggs, *Australian J. Chem.*, 1957, **10**, 128. (*e*) Kilpatrick and Arenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 3812. (*f*) Dippy and Williams, *J.*, 1934, 161. (*g*) Jeffery and Vogel, *ibid.*, p. 166. (*h*) Dippy and Lewis, *J.*, 1937, 1008.

The coefficients can be separated into several contributions: [7]

$$B = B_{\mathrm{HX}} + B_{\mathrm{Na,Cl}} - B_{\mathrm{Na,X}}$$

While the contributions $B_{\mathrm{Na,X}}$ will doubless be considerably different for acetic acid and the aromatic acids, it is probable that the largest source of difference resides in B_{HX}, the contribution of the un-ionized acid. Self-interaction and, to a smaller extent, salt effects, are known to have large effects on the activity coefficients of benzoic and phenylacetic acid,[8] and the self-interaction effect is larger for benzoic than for phenylacetic acid. Qualitatively the B parameters in Table 2 increase as the solubility of the acid in water decreases.

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[7] Guggenheim and Turgeon, *Trans. Faraday Soc.*, 1955, **51**, 747.

[8] Long and McDevit, *Chem. Rev.*, 1952, **51**, 119; Paul, *J. Amer. Chem. Soc.*, 1953, **75**, 2513.