2.273 at 25°)[2] was carried out in the usual way. The standardization was checked using pure carbon tetrachloride (2.227 at 25°).[2]

Instead of using values for $C_O$ and $C_L$ in each dielectric constant calculation, the following formula was derived for use in making the calculation directly from measurement recordings

$$e = 1 + (1.273)\,\frac{C' - C}{C' - C}$$

where $C$ is the capacity with nitrogen in the cell, $C'$ is the capacity with the liquid in the cell, and $C''$ is the capacity with benzene in the cell.

Gainesville, Florida

[Contribution from the Chemical Laboratory, University of New Brunswick]

# The Determination of the Rate Constants for the Recombination of Phenylglyoxylate Anions with Various Proton Donors

By K. Wiesner, Mary Wheatley[1] and J. M. Los

Received April 19, 1954

The recombination of phenylglyoxylate ions with protons was studied by measuring rate-controlled polarographic currents of the undissociated acid in the *p*H range in which the kinetic current is about 200 times smaller than the total diffusion current. The experimental data were found in full agreement with the theory based on participation of hydronium ions, water and boric acid as proton donors and the equations for fully rate-controlled currents developed earlier. The following values for individual rate constants of recombination were determined at 25°: $k_{H_3O^+} = 5.73 \times 10^{10}$ l. moles$^{-1}$ sec.$^{-1}$ $k_{H_2O} \times [H_2O] = 22$ sec.$^{-1}$, $k_{H_3BO_3} = 6.38 \times 10^2$ l. moles$^{-1}$ sec.$^{-1}$. While the accuracy of the values determined for $k_{H_3O^+}$ is approximately ±10%, the values for $k_{H_2O}$ and $k_{H_3BO_3}$ are accurate only to ±30% and thus indicate only the order of magnitude of these constants.

## Introduction

It was shown in the year 1946[2] that with acids, which gave rise in buffer solutions to separate polarographic waves of the undissociated acid and the acid anion, the *p*H at which the more positive wave of the undissociated acid becomes equal in height to the more negative wave of the anion may be shifted to higher values with respect to the *p*H of half-neutralization of the particular acid. This shift is a function of the recombination velocity of the particular acid anion with protons. In most cases the wave of undissociated acid is still obtained in solutions of such a *p*H that the undissociated acid can be present only in negligible concentration; in such instances the whole current due to the undissociated acid is kinetic in character.

If the concentrations of all the components of the system are constant,[3] an expression for the velocity constant may be obtained by substituting $\mu = {}^1/_2\sqrt{2D/k'}$ in the equation of Brdička and Wiesner[2] ($\mu$ = effective thickness of the interface, $D$ = diffusion constant, $k'$ = pseudo-unimolecular rate constant of the dissociation reaction). In a more complete mathematical analysis of the problem Koutecký and Brdička[4] have shown that for regions where the current of the undissociated acid is negligibly small the above expression is justified. The expression for $\mu$ as derived in this paper was $\mu = \sqrt{D/k'}$, and differs therefore only by the factor $\sqrt{2}$ from the one mentioned above.

The general equations of Koutecký and Brdička make it possible to calculate the ratio of the acid and anion wave for every *p*H including those where the acid wave is approaching in height the sum of both. For phenylglyoxylic and pyruvic acids the expected dependence of this ratio on the *p*H, calculated on the assumption that the only important mechanism of proton transfer is the reaction with hydronium ions, was given in the paper of Koutecký and Brdička.[4] It was found to deviate slightly but reproducibly from the experimental results.

Proton transfer in a buffered solution containing a reducible acid AH and a buffer acid BH may be expected to proceed through the following reactions

$$A' + H_3O^+ \underset{k_1'}{\overset{k_1}{\rightleftarrows}} AH + H_2O \qquad (I)$$

$$A' + H_2O \underset{k_2'}{\overset{k_2}{\rightleftarrows}} AH + OH' \qquad (II)$$

$$A' + BH \underset{k_3'}{\overset{k_3}{\rightleftarrows}} AH + B' \qquad (III)$$

Hanuš[5] has studied in detail the effect of buffer on the ratio of the acid and anion wave of phenylglyoxylic acid in the *p*H region in which both are of the same order of magnitude. He found that in this region the reaction III is negligible. He arbitrarily neglected reaction II and in effect assumed that proton transfer takes place by reaction I. Ruetschi and Trümpler[6] also neglected the action of proton donors other than hydronium ions. However the reason which these authors give for neglecting reaction II, namely, the approach of the kinetic current to zero in sufficiently alkaline solutions, is not correct.

## Experimental Part

It is shown in this communication that phenylglyoxylic acid (AH) gives, in borate buffer (at 25°)

---

(1) This paper is abstracted from a part of the thesis to be submitted by Mary Wheatley in partial fulfillment of the degree of Doctor of Philosophy.

(2) R. Brdička and K. Wiesner, *Chem. Listy*, **40**, 66 (1946).

(3) K. Wiesner, *ibid.*, **41**, 6 (1947).

(4) J. Koutecký and R. Brdička, *Collection Czech. Chem. Communs.*, **12**, 337 (1947).

(5) V. Hanuš, "Proceedings of the First Polarographic Congress in Prague 1951," Part I, Published by Přírodovědecké Vydavatelství, Prague, p. 811.

(6) P. Ruetschi and G. Trümpler, *Helv. Chim. Acta*, **35**, 1957 (1952).

in the region between $p$H 8 and 9.5, a precisely measurable wave of the undissociated molecule, $i_k$, of the order 0.1–5 × $10^{-6}$ amp. if the total concentration of the acid is 0.01–0.02 molar. Thus in this region $i_k$ is approximately 1/200 as large as the diffusion current of the anion and the application of the simple equation for $\mu$ is quite justified.

For the derivation of the equation expressing the dependence of $i_k$ on $p$H under the above conditions the following symbols were used

$[A']$ = concn. of Ph·CO·COO′ = $1.6 \times 10^{-2}$ moles/l. in all experiments
$[AH]$ = concn. of Ph·CO·COOH
$[BH]$ = concn. of boric acid
$[B']$ = concn. of borate ion
$K_B$ = dissociation constant of boric acid = $[H^+][B']/[BH]$
$K_W$ = ionic product of water = $[H^+]\cdot[OH']$
$C_B$ = analytical concn. of boric acid = $[B'] + [BH]$
$K_A$ = dissociation constant of phenylglyoxylic acid $= \frac{[H^+]\cdot[A']}{[HA]} = 5.9 \times 10^{-3}$
$\bar{q}$ = av. surface area/drop of mercury = $^3/_5 \times 0.85\ (m.t.)^{2/3}$
$m$ = outflow velocity of mercury = 0.001766 g. $\text{sec.}^{-1}$
$t$ = drop time of the electrode = 3.64 sec.
$D$ = diffusion constant of A′ or AH = $7.225 \times 10^{-6}$ $\text{cm.}^2\ \text{sec.}^{-1}$ (determined from the diffusion current by using the Ilkovič equation)
$F$ = 96,500 coulombs

($K_A$ was determined for the ionic strength 0.2 by measuring the half-neutralization point with a glass electrode; $f_{H_3O^+}$, the activity coefficient of $H_3O^+$, was taken as 0.80.[7])

If it is assumed that proton transfer occurs by the mechanisms I, II and III, then the kinetic current is given by (*cf.*[3,4])

$$i_k = 2F\bar{q} \times 10^{-3}[A']\mu[k_1[H_3O^+] + k_2[H_2O] + k_3[BH]] \tag{1}$$

where

$$\mu = \sqrt{D/(k'_1[H_2O] + k'_2[OH'] + k'_3[B'])} \tag{2}$$

The constants $k_1'$, $k_2'$ and $k_3'$ are related to $k_1$, $k_2$ and $k_3$ by the equilibrium conditions

$$k_1'/k_1 = [A'][H_3O^+]/[AH][H_2O] = K_A/[H_2O] \tag{3}$$

$$k_2'/k_2 = [A'][H_2O]/[AH][OH'] = K_A[H_2O]/K_W \tag{4}$$

$$k_3'/k_3 = [A'][BH]/[AH][B'] = K_A/K_B \tag{5}$$

If we substitute equations 3, 4 and 5 in equation 2 and the resulting expression for $\mu$ in equation 1 we obtain

$$i_k = 2F\bar{q} \times 10^{-3}[A']\sqrt{\frac{D}{K_A}}\left[k_1 + \frac{k_2[H_2O]}{[H_3O^+]} + \frac{k_3C_B}{[H_3O^+] + K_B}\right]^{1/2}[H_3O^+] \tag{6}$$

In equation 6 the only three unknowns are the rate constants $k_1$, $k_2$ and $k_3$ and the only variable is the hydrogen ion concentration. The value of $K_B$ is a function of the hydrogen ion concentration, apart from its dependence on the ionic strength.[8]

The change of $K_B$ with $[H_3O^+]$ was determined experimentally for the ionic strength used throughout this work (0.2) and is given in Fig. 1. Two experimental polarographic runs were done at 25° and are given in Fig. 2. For one of them (experimental points ⊙) $C_B$ = 0.2; for the other (experimental points △) $C_B$ = 0.05. The ionic strength throughout both runs was kept constant (0.2) by addition of sodium chloride.

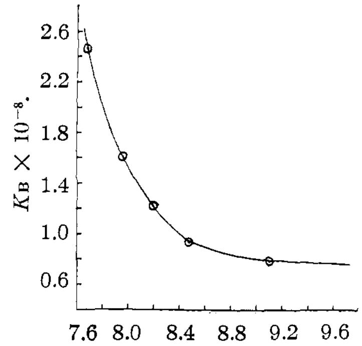

Fig. 1.—Dependence of the apparent boric acid dissociation constant on $p$H.

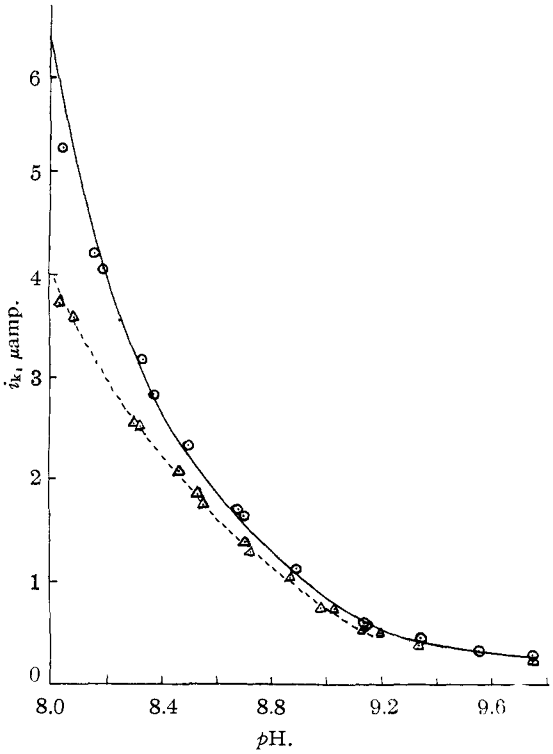

Fig. 2.—Dependence of the kinetic current of undissociated phenylglyoxylic acid on $p$H: ⊙, 0.2 $M$ borate; △, 0.05 $M$ borate; —, theoretical curve for 0.2 $M$ borate; ------, experimental curve for 0.05 borate; ionic strength of 0.05 $M$ borate made up to 0.2 $M$ with sodium chloride.

The $p$H values plotted were measured with a glass electrode and were converted into hydrogen ion concentrations by taking $f[H_3O^+] = 0.80$.

The solid curve in Fig. 2 is the theoretical curve obtained for the run with 0.2 $M$ borate from equa-

---

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950; p. 485, 488, 558, 562 and 601.

(8) B. B. Owen, THIS JOURNAL, **56**, 1695 (1934).

tion 6, if the following values for $k_1$, $k_2$ and $k_3$ are accepted

$$k_1 = 5.73 \times 10^{10} \text{ l. moles}^{-1} \text{ sec.}^{-1}$$
$$k_2[H_2O] = 22 \text{ sec.}^{-1}$$
$$k_3 = 6.38 \times 10^{2} \text{ l. moles}^{-1} \text{ sec.}^{-1}$$

The dotted curve is the experimental curve best fitting the 0.05 *M* borate run. The theoretical curve in this case has not been plotted since as will be clear from the sequel it cannot be expected to fit the experimental points. The method by which the above values of the rate constants have been arrived at will now be briefly outlined.

**The Determination of** $k_3$.—If equation 6 is squared we obtain upon subtraction for two different values of $C_B$ at the same *p*H

$$i_{k_1}{}^2 - i_{k_2}{}^2 = 4F^2 \times 10^{-6} (\bar{q})^2 \times \frac{D[A']^2}{K_A} (C_{B_1} - C_{B_2}) \frac{[H_3O^+]^2}{[H_3O^+] + K_B} \times k_3 \quad (7)$$

Thus if the values of $i_k$ are derived from the curves best fitting the experimental points in Fig. 2 (such a curve for the 0.2 *M* borate run is not drawn as it practically coincides, except for the last experimental point, with the theoretical curve) and if $i_{k1}{}^2 - i_{k2}{}^2$ is plotted against $[H_3O^+]/([H_3O^+] + K_B)$ a straight line going through the origin should result. The slope of this line is given by the expression

$$4F^2 \times 10^{-6} (\bar{q})^2 \times \frac{D}{K_A} [A']^2 (C_{B_1} - C_{B_2}) k_3$$

This plot is given in Fig. 3.

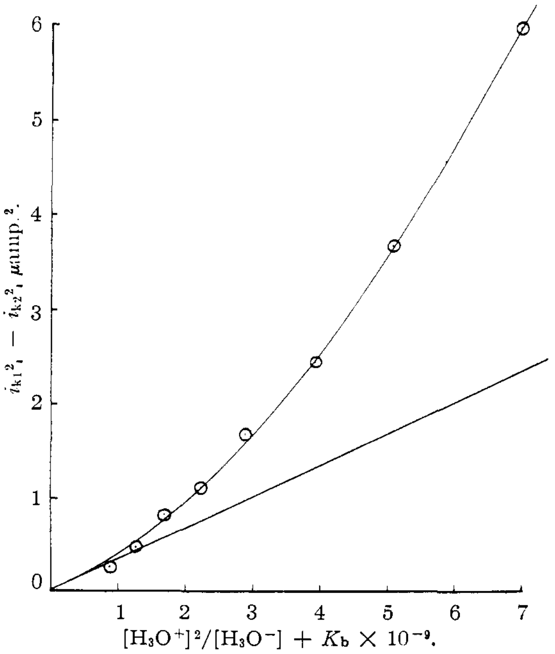

Fig. 3.—Determination of $k_3$.

In this plot the experimental points deviate progressively from the straight line drawn through the origin and the first two points. This straight line at the same time coincides with the tangent to the experimental curve at the origin. This deviation from the theory may however be readily explained. In the weakly buffered run (0.05 *M*) two effects occur when we proceed toward lower *p*H values: namely a decrease in the buffer action of boric acid while at the same time the increase in $i_k$ demands increasingly high buffering capacity. The $i_k$ values of the 0.05 *M* run are consequently lower than they should be and this effect increases with decreasing *p*H. Thus the slope of the straight line postulated by the theory may be derived by drawing the tangent through the origin. Figure 3 also shows that significant deviations from the straight line begin only at the third point on the curve proving that the buffering for the first two points is still satisfactory for both runs. The slope of the tangent through the origin was found $3.32 \times 10^8$ (microamp.)$^2$/(mole/liter). From this value $k_3$ was calculated: $k_3 = 6.38 \times 10^2$.

**Determination of** $k_1$ **and** $k_2$.—Values of $k_1$ and $k_2$ were determined by solving equation 6 for two experimental points of the 0.2 *M* buffer run. The points chosen were: *p*H 8.37, $i_k = 2.84 \times 10^{-6}$ amp.; and *p*H 9.14; $i_k = 0.598 \times 10^{-6}$ amp. Inserting these two values into equation 6, and putting $k_3 = 6.38 \times 10^2$, two equations are obtained with $k_1$ and $k_2$ as the only unknowns.

Thus these two values may be calculated: $k_1 = 5.73 \times 10^{10}$; $k_2(H_2O) = 22$. It is seen from Fig. 2 that the solid line which is the theoretical curve plotted on the basis of equation 6 and the values of the rate constants derived above fits the experimental points well within experimental error. It is possible that the highest point on the curve falls below the theoretical curve for the same reasons that cause the deviations in the weakly buffered run.

To estimate the precision of these values for $k_2[H_2O]$ and $k_3$ we have performed several runs in exactly the same way as described. The values for $k_3$ and $k_2[H_2O]$ for these independent runs were all well within 25% of the values reported. Consequently we believe that in spite of the limited precision of the method used in the determination of $k_3$ and the existence of complexes in boric acid solution the orders of magnitude of $k_3$ and $k_2[H_2O]$ are correctly determined. The value of $k_1$ on the other hand is very little affected by the limited precision of $k_2[H_2O]$ and $k_3$. If we for instance arbitrarily put $k_2[H_2O] = k_3 = 0$ and use an experimental point around *p*H 8.4 on the 0.2 *M* borate run, we obtain a value for $k_1 = 6.8 \times 10^{10}$ instead of $5.73 \times 10^{10}$. If on the other hand we plot the theoretical curve for $k_1 = 6.8 \times 10^{10}$; $k_2[H_2O] = k_3 = 0$ it becomes obvious that it does not fit the experimental data. The deviations are in this case several times greater than the difference between the 0.05 and 0.2 *M* runs and quite outside any experimental error. Consequently we may estimate the precision of the value for $k_1$ safely at least ±10% of the result.

## Discussion of Results

Hanuš[5] has tried to explain the deviations of the experimental results and the theoretical treatment of Koutecký and Brdička[4] by assuming a more complicated course of the dissociation reaction. The excellent agreement of the present results with theory shows that such assumptions are unnecessary. On the other hand it is clear from the values of our rate constants that in the *p*H region investigated by Koutecký and Brdička and Hanuš, the only important mechanism of proton transfer is indeed the reaction with hydronium ions as assumed by these authors. Therefore it is safe to assume that the deviation between experiment and theory in this region is caused by the difficulty to account precisely for the motion of the mercury drop in a solution containing concentration gradients. This difficulty of course does not exist when the concentrations of all components are constant, which are the conditions in the present work. In a recent communication which reached us after completion of this work Koutecký[9] has succeeded in accounting for the motion of the dropping electrode through the concentration gradients and has obtained excellent agreement between theory and experiment in the *p*H region in which $i_k$ and $i_d$ are of the same order of magnitude. His result is therefore in agreement with our conclusions. If the following values for the dissociation constants of water, hydronium ions and boric acid are accepted

$$K_{H_2O} = 10^{-14}/55.5;\ K_{H_3O^+} = 55.5;\ K_{BH} = 1.2 \times 10^{-9}$$

a logarithmic plot of the dissociation constant and the rate constant yields an approximately straight line for the three investigated proton donors. Thus it is seen that the Brönsted relation is reasonably well obeyed in this case. *This is the first time that the Brönsted relation has been verified for these primary proton transfer reactions.*

**Acknowledgments.**—We wish to thank the National Research Council, Ottawa, for support of this work. We are also grateful to the Leeds and Northrup Company for the loan of an Electrochemograph. We also wish to thank Professor F. J. Toole for his constant support and interest as well as for his help in writing this paper.

NEW BRUNSWICK, CANADA

---

[9] J. Koutecký, *Collection Czechov. Chem. Communs.*, **18**, 597 (1953).

---

# NOTES

## Solutions of Aluminum Chloride in Ethers

BY GORDON G. EVANS, THOMAS R. P. GIBB, JR., J. KEVIN KENNEDY AND FRANK P. DEL GRECO

RECEIVED MARCH 18, 1954

In connection with another problem, the conductivity of solutions of aluminum chloride in anhydrous ethyl ether and tetrahydrofuran has been studied. Since no further work is planned on these systems, the data are presented in their present form even though a full interpretation is not possible.

**Experimental.**—Pure solvent and concentrated stock solutions, dispensed from burets in an atmosphere of dry nitrogen, were run into a cylindrical vessel; conductances were measured by a pair of dipping electrodes, which were attached to a mercury-sealed, cam-driven shaft and served to stir the mixtures as well. The vessel was also provided with a rubber balloon, to accommodate the changes in gas volume due to the motion of the stirrer and the addition of liquid, and with a side-arm which permitted the removal of samples or insertion of a heavy rod to crush ampoules.

Commercial anhydrous ethyl ether was stored over sodium ribbon, decanted, refluxed overnight with a small amount of lithium aluminum hydride and distilled. Tetrahydrofuran was found to undergo significant decomposition when similarly treated, and was accordingly purified by fractional distillation from mineral oil to remove peroxides, storage overnight (not longer) over sodium and distillation from sodium. Aluminum chloride (Eimer and Amend reagent, anhydrous) was weighed out in a dry-box and dissolved under reflux (which the heat of solution of this powdered material necessitated); the resulting solutions were in the neighborhood of 0.3 *M*. Lithium chloride (Merck reagent, anhydrous) was dried overnight in a vacuum oven at 130° and loaded into ampoules in the dry-box. In operation, a known volume (usually 60 ml.) of solvent was run into the cell, the lithium chloride ampoule, if any, was broken under the surface of the solvent, and the aluminum chloride solution was then added gradually. Conductivities were measured at 1000 cycles with an Industrial Instruments conductivity bridge, model RC 16; for measurement of the lowest conductivities, it was necessary to extend the range of the instrument either by providing an additional fixed resistor in one arm of the bridge or by using a fixed resistor in parallel with the cell. The temperature was controlled within ±0.1° within any single run, but varied from 17 to 23° in different runs.

**Results.**—From a quantitative viewpoint, the data are not entirely reproducible, the conductances measured in ethyl ether solution showing variations up to about ±15%. (In tetrahydrofuran the variation is even more pronounced; see below.) The shapes of the curves, however, are quite uniform. The results of typical experiments are shown graphically in Figs. 1 and 2, and the conclusions reached may be stated as follows.

(1) The curve of specific conductance *vs.* concentration for solutions of aluminum chloride in ethyl ether is concave *upward*. Correspondingly, the equivalent conductance increases with increasing concentration, a fact which indicates that the ionization process is a complicated one involving at least two molecules of aluminum chloride and probably the solvent as well.

(2) The conductivity of a suspension of anhydrous lithium chloride in ethyl ether is very low, little greater than that of the ether itself. The addition of an aluminum chloride solution to such a suspension, however, results in specific conductances much higher than those observed with aluminum chloride alone, and the curvature of the graph is more pronounced. Presumably the equilibrium $AlCl_3 + LiCl\ (solid) \rightleftarrows Li^+ + AlCl_4^-$ is established; but, inasmuch as only a small part of the lithium chloride is brought into solution by the addition of an equimolar amount of aluminum chloride, it appears that the left-hand side of the equilibrium is strongly favored. (The arrow in