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Kinetics of Dehydration of Aromatic Aldehydes Determined by the Rotating Disc Electrode Technique

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The rate constant for the irreversible dehydration of a number of aromatic aldehyde hydrates has been measured. The hydrates were generated by constant potential electrolysis of the respective aromatic acid at a rotating disc electrode. The aldehydes are then further reduced to the alcohol. The rate constant can be calculated from the ratio of the concentration of intermediate aldehyde to the total concentration of products.

The theory was further extended to include the reverse hydration of the aldehyde to the hydrate and applied in the case of *m*-chlorobenzaldehyde. A value for the equilibrium constant of $K = 1.30 \pm 0.25$ was obtained for this reaction.

On a mesuré les constantes de vitesse pour la déshydratation irréversible d'un certain nombre d'hydrates d'aldéhydes aromatiques. Les hydrates étaient formés par électrolyse à potentiel constant des acides aromatiques correspondants utilisant une électrode à disque rotatif. Les aldéhydes peuvent être réduits jusqu'au niveau de l'alcool. Les constantes de vitesse peuvent être calculées à partir des rapports de concentration de l'aldéhyde intermédiaire sur la concentration totale des produits.

On a élargi la théorie de façon à inclure l'hydratation de l'aldéhyde pour reformer l'hydrate et cette théorie a été appliquée au cas du *m*-chlorobenzaldéhyde. On a obtenu une valeur de $K = 1.30 \pm 0.25$ pour la constante d'équilibre de cette réaction.

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[1]

Introduction

A method for determining the rate constant, k_2 , for a chemical reaction coupled to an electrochemical reaction using the technique of

constant potential electrolysis at a rotating disc electrode has been published (1). The method was applied to the electroreduction of aromatic carboxylic acids (2), an example of the common ECE mechanism:



Where k_e , k_2 , and β represent the rate constants for the respective steps. The constant, k_e ,

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The theory developed (2), was, however,

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erroneously applied, and the data used were suspect due to the low buffer capacity employed. In the present communication the previously derived theory was reapplied to results obtained under more controlled conditions.

Since such dehydration reactions have been shown to be reversible (2) an attempt to include this reversibility has been made. However only in the case of m-chlorobenzaldehyde was such an extension found to be feasible.

Theory

The advantage of using the rotating disc electrode is that the rate of convective diffusion of species to and from the electrode surface can be accurately controlled. Diffusion of species can be confined to a narrow layer of solution of thickness δ close to the electrode surface, where δ is given by (3)

$$\delta = 1.80 D^{1/3} v^{1/6} \omega^{-1/2}$$

where D is the diffusion coefficient (cm² s⁻¹) of the diffusing species, v the solution kinematic viscosity in (kg m⁻¹ s⁻¹) × 10⁻¹ and ω the angular rotation speed of the electrode in radians s⁻¹.

The rate constant for mass transfer is given by (4)

$$\beta = DA/V \delta s^{-1}$$

where A is the electrode area (cm^2) and V the solution volume (cm^3) .

The first electron transfer can be controlled by the rate of diffusion or the rate of electron transfer depending on the electrode potential. The second electron transfer is assumed to be always diffusion controlled at the potentials necessary to initiate step 1. The volume of solution is assumed large compared to that of the diffusion layer and the chemical step only takes place outside the diffusion layer.

A number of different experimental conditions are possible; each necessitating a slightly different theoretical model.

1. Chemical Step - Irreversible

The theory for this situation has been published (1). Two sets of experimental conditions are possible.

(a) The potential is cathodic enough to make the first electron transfer step diffusion controlled.

(b) The reactant concentration is high and the

electrode potential low so that the first electron transfer step is controlled by the heterogeneous electrochemical rate. If the degree of conversion of reactant to products is maintained below $\simeq 5\%$ then the reactant concentration can be taken as constant throughout the experiment.

Condition (b) was applied in the present paper and values of k_2 were calculated using the derived expression for the ratio of concentrations, R, defined by (2)

[4]
$$R = \frac{C_{\rm B}{}^{\rm b} + C_{\rm c}{}^{\rm b}}{C_{\rm B}{}^{\rm b} + C_{\rm c}{}^{\rm b} + C_{\rm D}{}^{\rm b}}$$
$$= \frac{\beta^2 - k_2{}^2 - 2k_2\beta \exp(-\beta t) + k_2{}^2 \exp(-\beta t)}{2\beta^2 + tk_2\beta^2 - t\beta k_2{}^2 - 2k_2\beta}$$

where C_x^{b} are the bulk solution concentrations of the respective species.

Previously (2) the expression

[5]
$$k_2 \propto (R - \exp(-\beta t))$$

was used to estimate the value of k_2 . The proportionality constant for eq. 5 was calculated using a value of k_2 for benzaldehyde estimated from the data presented in Figs. 2 and 5 of ref. 2. k_2 for the other aldehydes was then calculated from eq. 5 by comparing the ratio Rof that aldehyde at a number of values of βt , to the value of R for benzaldehyde at the same value of βt .

Equation 5 was obtained from eq. 4 by neglecting all the squared constant terms and limiting the analysis to times such that the linear terms in t can also be neglected.

The terms in k_2^2 and β^2 cannot, however, be eliminated since they are of the same order of magnitude as the exponential terms.

Values of k_2 calculated using relationship [5] indicate that the rates of dehydration are in the following order for a series of ring-substituted aromatic acids:

$$m$$
-Cl > o -Cl > benzoic > o -CH₃ > o -OH

This is contrary to the order expected on the basis of substituent effects. Also relationship [5] implies that the largest instantaneous concentration of intermediate will be attained with the fastest rate of dehydration. This is opposite to the predictions of the theory presented (2).

2. Chemical Step - Reversible

The theory for the reversible case will only be solved for the experimental conditions actually

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[20]

applied. These correspond to the assumptions of 1(b) above. The theory could be simply extended to include case 1(a) if necessary.

The scheme for the present situation can be written as follows

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = 0$$

[7]
$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = k_{\mathrm{e}}(C_{\mathrm{A}}{}^{\mathrm{b}})_{\mathrm{i}} - k_{\mathrm{f}}C_{\mathrm{B}}{}^{\mathrm{b}} + k_{\mathrm{b}}C_{\mathrm{c}}{}^{\mathrm{b}}$$

[8]
$$\frac{\mathrm{d}C_{\mathrm{c}}^{\mathrm{b}}}{\mathrm{d}t} = k_{\mathrm{f}}C_{\mathrm{B}}^{\mathrm{b}} - k_{\mathrm{b}}C_{\mathrm{c}}^{\mathrm{b}} - \beta C_{\mathrm{c}}^{\mathrm{b}}$$

$$[9] \qquad \qquad \frac{\mathrm{d}C_{\mathrm{D}}^{\mathrm{b}}}{\mathrm{d}t} = \beta C_{\mathrm{c}}^{\mathrm{b}}$$

Equations 6 to 9 are subject to the following conditions

[10] At
$$t = 0$$
; $C_A^{\ b} = (C_A^{\ b})_i$

$$[11] (C_B^{\ b})_i = (C_c^{\ b})_i = (C_D^{\ b})_i = 0$$

At t > 0, $x = \delta$, all concentrations are equal to their bulk solution concentrations.

 $(C_x)_i$ refers to the initial concentration of species X.

The above scheme can be solved by simple integration and by Laplace Transform to yield:

$$[12] \quad C_{\rm B}^{\ b} = k_{\rm c}(C_{\rm A}^{\ b})_{\rm i} \left[\frac{k_{\rm b} + \beta}{\alpha \gamma} + \frac{(k_{\rm b} + \beta - \alpha)}{\alpha(\alpha - \gamma)} \exp(-\alpha t) + \frac{(k_{\rm b} + \beta - \gamma)}{\gamma(\gamma - \alpha)} \exp(-\gamma t) \right]$$

$$[13] \quad C_{\rm c}^{\ b} = k_{\rm f} k_{\rm e}(C_{\rm A}^{\ b})_{\rm i} \left[\frac{1}{\alpha \gamma} + \frac{\exp(-\alpha t)}{\alpha(\alpha - \gamma)} + \frac{(k_{\rm b} + \beta - \gamma)}{\alpha(\alpha - \gamma)} + \frac{(k_{\rm b} + \beta - \gamma)}{\alpha(\alpha - \gamma)} + \frac{(k_{\rm b} + \beta - \gamma)}{\alpha(\alpha - \gamma)} \right]$$

$$+ \frac{\exp(-\gamma t)}{\gamma(\gamma - \alpha)}$$

[14]
$$C_{\rm D}^{\rm b} = \beta k_{\rm f} k_{\rm c} (C_{\rm A}^{\rm b})_{\rm i} \left[\frac{t}{\alpha \gamma} + \frac{(1 - \exp(-\alpha t))}{\alpha^2 (\alpha - \gamma)} + \frac{(1 - \exp(-\gamma t))}{\gamma^2 (\alpha - \gamma)} \right]$$

where

[15]
$$\alpha = 0.5[\theta + (\theta^2 - 4\beta k_f)^{1/2}]$$

[16] $\gamma = 0.5[\theta - (\theta^2 - 4\beta k_f)^{1/2}]$
and
[17] $\theta = (k_f + k_b + \beta)$

The ratio, R, defined by the first equality in eq. 4 will be independent of both k_c and $(C_A{}^b)_i$.

Computation of eqs. 12 and 13 shows that the individual values of $C_{\rm B}{}^{\rm b}$ and $C_{\rm c}{}^{\rm b}$ become constant for larger values of βt . Under these conditions $dC_{\rm B}{}^{\rm b}/dt$ and $dC_{\rm c}{}^{\rm b}/dt$ (eqs. 7 and 8) are both equal to zero; hence

[18]
$$\frac{\mathrm{d}C_{\mathrm{c}}^{b}}{\mathrm{d}t} = 0 = k_{\mathrm{f}}C_{\mathrm{B}}^{b} - k_{\mathrm{b}}C_{\mathrm{c}}^{b} - \beta C_{\mathrm{c}}^{b}$$

which leads to the relationship

[19]
$$\frac{C_{\rm c}^{\rm b}}{C_{\rm B}^{\rm b}} = \frac{k_{\rm f}}{(k_{\rm b} + \beta)}$$

For $k_{\rm b} \gg \beta$, eq. 19 reduces to

$$\frac{C_{\rm c}^{\rm b}}{C_{\rm B}^{\rm b}} = \frac{k_{\rm f}}{k_{\rm b}}$$

Under these conditions the ratio of hydrate to aldehyde should be independent of electrode rotation speed.

For $k_{\rm b} \ll \beta$, eq. 19 becomes

$$[21] \qquad \qquad \frac{C_{\rm c}^{\rm b}}{C_{\rm B}^{\rm b}} = \frac{k_{\rm f}}{\beta}$$

which is equivalent to the irreversible case.

Equation 19 offers a simple means of separating k_f and k_b . For large enough values of βt the slope of the plot of alcohol concentration (C_D^b) against t should be linear yielding an estimate of C_c^b . C_B^b can then be obtained from the analyzed yield of aldehyde, $C_B^b + C_c^b$. If the analysis is repeated for a number of β values, k_f and k_b can be calculated.

The consistency of the values obtained could be checked in the following manner. Using the values of k_f and k_b as calculated by the above method a value of the equilibrium constant, K, can be used to compute the theoretical product ratio, R, as a function of βt for a series of k_f values. Comparison with the experimental ratio would then enable k_f and k_b to be calculated.

Previously (2) the separation of k_2 into k_f and k_b was affected using the equation

[22]
$$k_2 C_{\rm B}^{\ b} = k_{\rm f} C_{\rm B}^{\ b} - k_{\rm b} C_{\rm c}^{\ t}$$

For short times

$$[23] k_2 \simeq k_{\rm f}$$

Equation 23 can be shown to apply, under the present conditions, only in the time interval

 $t \leq 1$ h; a range which is experimentally difficult to investigate.

The method employed in this paper however uses the data obtained over the whole time range of the electrolysis.

Experimental

The experimental method previously applied (2) was again used to follow the concentrations of products. Since the theory is based on the conversion of less than 5% of reactant to product the use of an "*in situ*" technique such as i.r. spectroscopy is subject to the disadvantage that the signals from the products are swamped by that of the reactant. Since concentrations of products rarely exceed 10^{-3} M in solution, quantitative analysis using n.m.r. was not considered.

Because both aldehyde and alcohol concentrations must be known as a function of time, any method of data acquisition not involving an interruption of the electrolysis current necessitates a sampling technique.

G.l.c. was deemed the most useful technique to quantitatively separate the products from reactant since in this case treatment of the sample to remove excess unreacted acid was not necessary.

I.r. spectroscopy was found to be useful only in the case of salicylic acid, where the aldehyde and alcohol absorbances are sufficiently distinct to be used for analysis. Even in this case error is introduced by the necessity to remove unreacted salicylic acid.

The experimental set-up and electrode design have been previously described (2). A number of modifications were incorporated into the experimental procedure and these are explained below.

Working Electrode

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In the present work the electrode, once prepared by electroplating mercury on copper from acidic $Hg(NO_3)_2$, was stored under mercury between runs, replating being unnecessary. On storing, copper amalgam separated out on the surface of the electrode but could be removed by excess mercury. This method of electrode maintenance led to better reproducibility than if the surface was replated between each run.

The condition of the electrode surface changed slightly over the period of a long (9 h) electrolysis. This can be seen by the change in Tafel slope and the lowering of the overvoltage in 1 N HCl, Fig. 1. The slightly lower overvoltage on the plated electrode can be accounted for by the catalytic action of copper dissolved in the mercury (8). Figure 1, plots 3 and 4, indicate that the electrode deteriorates somewhat throughout the electrolysis.

Apparatus

Constant potential electrolyses were performed using a potentiostat (Wenking Model 70 HP 10 or Chemical Electronics Type TR 70-2A) and a Beckmann Rotating Disc electrode unit. Chemical analyses were performed on an F and M 402 Gas Chromatograph using a silicone gum rubber SE52 column, and on a Unicam SP 800 u.v. spectrophotometer.

Analysis

The main analytical method was g.l.c. as previously reported (2). The products from the electrolysis of



FIG. 1. Steady-state current Voltage plots recorded in 1 N HCl for various electrode conditions; (1) pure Hg pool electrode, Tafel slope = 120 mV; (2) Cu electrode, 170 mV; (3) mercury-plated copper electrode prior to electrolysis; 140 mV; (4) plated electrode after a 3 h electrolysis, 150 mV.



FIG. 2. U.v. characteristics of peaks used for analysis of electrolyzed salicylic acid solutions.

salicylic acid were analyzed by u.v. spectrophotometry. Figure 2 shows the absorbance characteristics.

The products were extracted into ether, and analyzed directly. In the case of salicylic acid the extract was neutralized with sodium carbonate to remove the acid. The acid was then estimated from the salicylate anion absorbance in aqueous solution. In all other cases the acid was estimated using g.l.c. as the methyl ester formed by reaction with diazomethane (5).

Product identification has been previously described (2). However identification of the alcohols by re-oxidation to the acid was inconclusive. A more positive identification was achieved by constant potential electrolysis of a standard aldehyde sample at the rotating disc electrode, at potentials on the plateau of the waves attributed to the reduction of aldehyde to alcohol (6, 7). Coulometric analysis showed that in all cases reported the number of electrons transferred $n = 2 \pm 0.2$. The g.l.c. peaks obtained from the products coincided with those attributed to alcohol in the reduction of the acid at higher potentials. Further evidence was obtained by a second electrolysis of the sample (already electrolyzed) at lower

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ALDEHYDE VIELD + 10 Males

potentials where only Step 3 could occur (i.e. aldehyde

2e+2H+2e+2H+ alcohol). Subsequent g.l.c. analysis showed the aldehyde peak to have disappeared and the alcohol peak to have increased.

Chemicals

The aromatic acids were from Eastman Kodak (Highest Purity) and were used without further purification. The phosphate buffers were BDH (Analar grade) as was the HCl and boric acid.

Solutions

The composition of the solutions was as follows; 0.6 M KCl; 0.8 M phosphate buffers to pH 6.2; 0.1 M aromatic acid. Where necessary the pH was adjusted to 6.2 using 1 N HCl or 1 N NaOH. In the electrolysis of salicylic acid KCl was 0.35 M and H₃BO₃ 0.25 M. The conditions for salicylic acid were identical to those used previously. During experiments at high buffer capacity the pH was maintained by manual addition of HCl at regular intervals. This was necessary because of the simultaneous hydrogen evolution.

Choice of Experimental Conditions

In order to obtain reasonably high concentrations of products a sufficiently cathodic potential was necessary.

However, increasing the potential cathodically led to a large increase in the hydrogen evolution current. This had two effects. First the condition of the electrode deteriorated. This could be observed by a test similar to that demonstrated in Fig. 2. Secondly if the evolution of gas bubbles was too copious the results obtained became erratic.

Results and Discussion

Figures 3 and 4 show the aldehyde and alcohol yields as a function of time for a number of aromatic carboxylic acids studied. Unlike the aldehyde yields obtained previously (2), the present plots, Fig. 3, attain a plateau value as predicted by the theory.

Figure 5 shows the product ratio analyzed according to the irreversible scheme with the conditions stated in section 1(b) of the theory. The values of k_2 taken from this figure are tabulated in Table 1.

The values of k_2 for benzoic acid and p-CH₃ benzoic acid can only be considered as order of magnitude estimates since they are close to the limits of applicability of the theory. The plot for salicylic acid was outside the range of the theory, and no value for k_2 can hence be estimated.

Similar plots to those of Fig. 5 for data obtained in solutions of low buffer capacity (2) fall below the plots obtained in the present work. For benzaldehyde and p-methylbenzaldehyde they fall outside the range of the theory. The



various aromatic carboxylic acids $\beta = 10^{-4} \text{ s}^{-1}$ ($\omega =$ 2300 r.p.m.). •, m-chlorobenzoic acid electrolyzed at E = -1.95 V; \blacksquare , benzoic acid, E = -1.95 V; O, salicylic acid, E = -1.95 V; $\mathbf{\nabla}$, *p*-methylbenzoic acid, E = -2.01 V; \Box , o-chlorobenzoic acid, E = -2.01 V.



FIG. 4. Alcohol yields as a function of time. Legend same as Fig. 3.

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TABLE 1.	Values of the rate constant k_2	N•	

Compound	k2
Benzoic acid p-CH ₃ benzoic o-Cl benzoic m-Cl benzoic	$ \begin{array}{c} \sim 10^{-2} \text{ s}^{-1} \\ \sim 10^{-2} \text{ s}^{-1} \\ 6 \times 10^{-4} \text{ s}^{-1} \\ (1.5 \text{ to } 2.0) \times 10^{-4} \text{ s}^{-1} \end{array} $



FIG. 5. Data of Fig. 3 and Fig. 4 plotted according to eq. 3 for the irreversible case. \bullet , *m*-chlorobenzoic acid; \blacksquare , *o*-chlorobenzoic acid; \blacktriangledown , benzoic acid; \square , *p*-methyl benzoic acid; \bigcirc , salicylic acid. Plots are theoretical curves for varying values of k_2 ; (1) 10^{-5} s^{-1} ; (2) 2 × 10^{-5} ; (3) 4 × 10^{-5} ; (4) 8 × 10^{-5} ; (5) 1.6 × 10^{-4} ; (6) 3.2 × 10^{-4} ; (7) 6.4 × 10^{-4} ; (8) 1.024 × 10^{-2} ; (9) 1.024.

effect of the buffer capacity on the product ratio for benzaldehyde is shown in Fig. 6.

For the values of k_2 , tabulated above, to be meaningful the product ratio must be independent of the buffer capacity. Unfortunately attempts to obtain data at higher buffer capacities were frustrated for the reasons stated in the experimental section.

However, confidence can be placed in the present results for the following reasons.

1. The concentration of intermediates attains a plateau when plotted as a function of βt .

2. Chemical analysis indicated yields in the range 85% to 90%, except in the case of salicylic acid. No dimeric or polymeric products were detected. Such an analysis, however, can only be considered approximate since it involved a calculation made on a very small conversion of reactant to products. Percentage yields based on synthetic scale experiments (9) were in the range 70 to 80%, indicating a substantial loss of reactant via side reactions. However the last experiments were performed with much smaller buffer capacities than those employed in the



FIG. 6. Product Ratio, R, for electrolysis of benzoic acid at E = -1.95 V in phosphate buffers (pH 6.2) for varying total buffer concentrations. (1) 0.8 M total buffer concentration + manual pH adjustment with 1 N HCl. (2) 0.15 M total buffer concentration + manual pH adjustment. (3) 0.074 M total buffer concentration + no adjustment.

present work, in order to obtain high current efficiencies.

3. The coulometric experiments performed on the aldehydes yielded values for n = 2.0 + 0.2. This indicates that the conversion of aldehyde to alcohol proceeds efficiently with very little loss of material in side reactions. Hence any significant loss of material in the overall reduction of acid to alcohol must occur in the first electron transfer step. However the calculation of k_2 is independent of the rate of this step and only requires that it be constant. Hence loss of material in side reactions at this stage of the process will not affect the calculation of the chemical rate constant, providing the rate of production of intermediates is constant. That this is in fact the case can be seen by plotting the total product yield, $C_{\rm B}{}^{\rm b} + C_{\rm c}{}^{\rm b} + \tilde{C}_{\rm D}{}^{\rm b}$, as a function of time. Straight lines passing through the origin were obtained in all cases except that of salicylic acid. The slope of such a plot would in fact yield a value for $k_{\rm c}$. Deviations from linearity were observed for previously obtained, Figs. 1 and 16 of ref. 2.

For the solutions of low buffer capacity, Fig. 6 plots 2 and 3, the aldehyde yields showed a peak when plotted against the electrolysis time. This could be accounted for by a decrease in the electrochemical rate for the first electron transfer step. This was also indicated by a corresponding decrease in the rate of production of alcohol and a fall in the percentage yield. The amount of acid converted to products,



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TABLE 2. Data for *m*-chlorobenzoic acid at -1.95 V

ω(r.p.m.)	δcm	β s ⁻¹	C_{c}^{b}/C_{B}^{b}	$k_{\rm f}$ and $k_{\rm b}$ (s ⁻¹ × 10 ⁴)
(a) 500	2.25×10^{-3}	4.64×10^{-5}	1.10	$(k_{\rm f}; 4.82; 10.78; 2.65)$
(b) 1285	1.40×10^{-3}	7.5×10^{-5}	1.07	$(k_{\rm b}; 3.92; 10; 1.70)$
(c) 2300	1.05×10^{-3}	10-4	0.98	(K; 1.23; 1.08; 1.56)

[25]

however, did not fall substantially, as demonstrated by the analysis of unreduced acid.

Hence the main effect of low buffer capacity would appear to be to cause a local pH increase close to the electrode surface, leading to possible dimerization or polymerization products, rather than a decrease in the electrochemical rate.

A similar decrease in the aldehyde to alcohol ratio was noted at low pH values. In this case the ratio was not only dependent on the buffer capacity but was reduced even in well buffered solutions. This can be attributed to acid catalysis, leading to a large proportion of the chemical reaction taking place within the diffusion layer:



The data obtained for salicylic acid did not permit the calculation of a value for k_2 . Possible explanations for this are:

1. k_2 is very fast and a substantial degree of conversion of hydrate to aldehyde occurs within the diffusion layer. This would lead to an increase in the rate of diffusion of the aldehyde back to the electrode and hence a smaller proportion of aldehyde in the total analysed product.

2. The estimated yield of product in the case of salicylic acid was around 70% under the conditions employed, indicating a possible loss of products to dimers and polymers.

3. In the u.v. analysis for salicyl alcohol, unreduced acid was removed by treating the other extracts with dilute aqueous alkali. Loss of salicylaldehyde, which is soluble in alkali, could be observed by the decrease in its u.v. absorbance on successive treatments. The alcohol absorbance was unaffected.

Reversible Analysis

Equation 19 offers a means of examining the reversibility of the dehydration reaction. Variation of the angular velocity of the electrode, and hence β , should yield data from which k_f and k_b can be calculated. However only in the case of *m*-chlorobenzaldehyde were the product yields sufficiently high to give reproducible changes in product ratio with changes in β .

In the case of benzoic acid the experimental product ratio was insensitive to changes in β . This is equivalent to the condition expressed by eq. 20. Hence

$k_{b(benzoic)} \gg \beta$

This is not a surprising result considering that when treated as irreversible the dehydration rate constant, k_2 , is at the upper limit of measurement for the theory.

For *o*-chloro- and *p*-methylbenzoic acids the product yields were too small to yield meaningful changes in product ratio on changing β . This could be improved by an increase in cathodic potential. However this leads to scattered data for the reasons stated in the experimental section.

The results for *m*-chlorobenzaldehyde are listed in Table 2, yielding the $k_{\rm f}$ and $k_{\rm b}$ values shown.

The values of $k_{\rm f}$, $k_{\rm b}$ show a large spread when determined by this method. However, the equilibrium constants calculated on the basis of these values are quite accurate and can be used to calculate more accurate value for $k_{\rm f}$ and $k_{\rm b}$.

The data of Table 2 lead to the value

$K = 1.30 \pm 0.25$

Using a value of K = 1.3 a series of product ratio calibration plots were constructed. Fig. 7 shows the experimental data and the closest fitting theoretical curve, yielding

$$k_{\rm f} = (6.5 \pm 1.5) \times 10^{-4} \,{\rm s}^{-1}$$

 $k_{\rm h} = (4.2 \pm 1.0) \times 10^{-4} \,{\rm s}^{-1}$

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FIG. 7. Product ratio as a function of βt for the three runs listed in Table 2; ×, $\omega = 2300 \text{ r.p.m.}$; \blacksquare , $\omega = 1285 \text{ r.p.m.}$; \bigcirc , $\omega = 500 \text{ r.p.m.}$ The plot represents the theoretical curve for $K = 1.30, k_{f} = 6.5 \times 10^{-4}, s^{-1}$ for the reversible case (b) (see Theory section).

The error limits were estimated by constructing calibration curves for K = 1.05 and 1.55 and computing maximum and minimum values of $k_{\rm f}$ and $k_{\rm b}$. This, taken together with the spread of data around the theoretical product ratio, leads to the estimated errors quoted above.

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