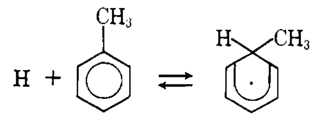
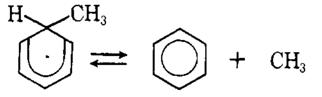
Table II. Pyrolysis of 1,3-CH with Added $C_6D_6$ or $PhCH_3$ at 391°

| Initial pressures, torr 1,3-CH | $C_6D_6$ | $PhCH_3$ | Length of run, $10^3$ sec | Relative yields $H_2$ | HD | $CH_4$ | $k_5/k_{12}$ | $k_5/k_{16}$ |
|---|---|---|---|---|---|---|---|---|
| 10 | 40 | | 5 | 100 | 11.1 | | 3.6 | |
| 40 | 40 | | 1.8 | 100 | 3.4 | | 2.7 | |
| 20 | | 10 | 1.8 | 100 | | 11 | | 2 |

When toluene is added initially to 1,3-CH, methane is produced. This may be explained[11] by eq 16–19.



(16)



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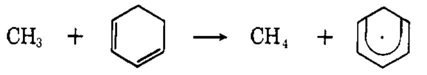

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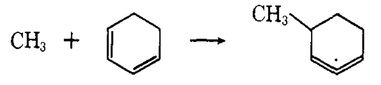
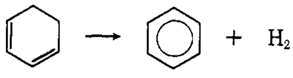


(19)

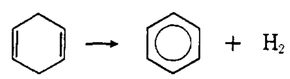
From thermochemistry at 391°, $K_{16}K_{17} = 10^{4.5}$, and, as $k_{16}/k_{-17}$ is unlikely to be greater than $10^{2.5}$, then $k_{17}/k_{-16} = 10^2$. That is the error in assuming $R_{16} = R_{17}$ is about 1% and may be neglected. No value has been reported for $k_{18}/k_{19}$, but from the results of Gresser, Rajbenbach, and Szwarc,[12] and also James and Suart[9,10] $k_{18}/k_{19}$ can be estimated to be equal to 1. Then, $k_5/k_{16} = R_{H_2}[PhCH_3]/2R_{CH_4}[CH] \sim 2$. Thus, at 391°, $k_{12}:k_{16}:k_5:k_6 = 1:1.5:3:12$.

**Unimolecular Elimination of Hydrogen from 1,3-CH.** From the constancy of the ratio $R_{H_2}/R_{\text{cyclohexene}}$ over the temperature range, it may be deduced that the unimolecular elimination of hydrogen from 1,3-CH contributes less than 10% to the yield of hydrogen; that is, $R_{20} < 10^{-8}$ mole l.$^{-1}$ sec$^{-1}$ at 391° and 40 torr, and $k_{20} < 10^{-5}$ sec$^{-1}$. From the measured[3] rate of reaction 21, $k_{21}/k_{20}$



(20)

$> 10^3$, so, if $A_{21} \sim A_{20}$, $E_{20} - E_{21} > 9$ kcal mole$^{-1}$, and, as $E_{21} = 44$ kcal mole$^{-1}$, then $E_{20} > 53$ kcal mole$^{-1}$.



(21)

The marked difference in the rates of thermal unimolecular elimination of hydrogen from 1,3-CH and 1,4-CH is in line with the theoretical predictions of Hoffmann.[4]

**Acknowledgment.** We thank Dr. R. D. Suart for communication of his results prior to publication, Miss J. S. Whittick and Mr. F. M. Church for mass spectrometric analyses, and Miss E. A. Lawler and Mr. L. J. Salas for preparative gas chromatographic purifications.

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[11] M. Szwarc, *J. Chem. Phys.*, 17, 128 (1948).

[12] J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Am. Chem. Soc.*, 83, 3005 (1961).

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# The Kinetics of Competitive-Consecutive Second-Order Reactions Involving Difunctional Unsymmetrical Molecules. The Kinetics of the Alkaline Hydrolysis of Diethyl Malate

**W. J. Svirbely and Frederick A. Kundell**[1]

*Contribution from the Chemistry Department, University of Maryland, College Park, Maryland.*
*Received April 8, 1967*

**Abstract:** A kinetic process of a four-step competitive-consecutive second-order reaction involving an unsymmetrical difunctional molecule can be written as A + B → C + M, A + B → E + M, A + C → P + M, and A + E → P + M, having the rate constants $k_1$, $k_2$, $k_3$, and $k_4$, respectively. The rate equations have been solved in terms of the variable λ where $\lambda = \int_0^t A\,dt$. The solution is of the form $A/B_0 = G_1e^{-(k_1 + k_2)\lambda} + G_2e^{-k_3\lambda} + G_3e^{-k_4\lambda} + (A_0/B_0) - 2$, where the $G$'s are constants involving various combinations of $k_1$, $k_2$, $k_3$, and $k_4$. A least-squares solution can be used which allows the calculation of the $k$'s. The procedure was used to determine the $k$'s for the alkaline hydrolysis of diethyl malate, an unsymmetrical diester containing a hydroxyl group, in dioxane–water mixtures of varying composition at several temperatures. A mechanism involving the inductive effect of the hydroxy substituent is postulated for the reaction, and each of the $k$'s is assigned to a particular step in the reaction. The various thermodynamic activation values have been calculated.

During the past few years, there have appeared from our laboratory a series of papers concerned with the kinetics of competitive-consecutive second-order reactions involving multifunctional symmetrical compounds.[2] Our investigations have been extended to kinetic studies of difunctional and trifunctional unsym-

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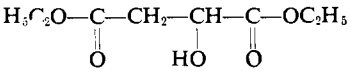
[1] Abstracted from a thesis submitted by F. A. Kundell to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] (a) W. J. Svirbely, *J. Am. Chem. Soc.*, 81, 255 (1959); (b) W. J. Svirbely and H. E. Weisberg, *ibid.*, 81, 257 (1959); (c) W. J. Svirbely and J. A. Blauer, *ibid.*, 83, 4115, 4118 (1961); (d) J. A. Blauer, L. Schmid, and W. J. Svirbely, *ibid.*, 85, 2716 (1963); (e) W. J. Svirbely and A. D. Kuchta, *J. Phys. Chem.*, 65, 1333 (1961); (f) W. J. Svirbely and P. A. Cunniff, *Can. J. Chem.*, 40, 1826 (1962).

metrical compounds. In this paper, we shall report on the alkaline hydrolysis of diethyl malate, an unsymmetrical diester. In a later paper, we shall report on the alkaline hydrolysis of triethyl citrate, an unsymmetrical triester.

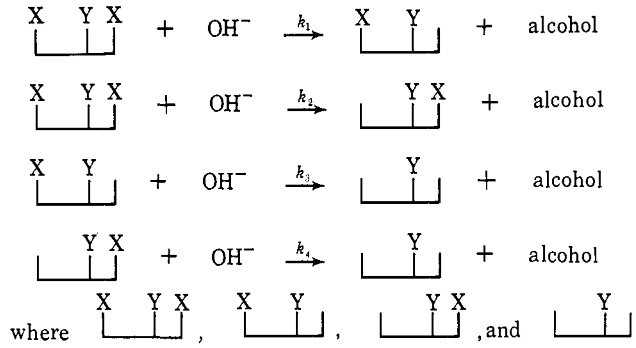
Diethyl malate is an unsymmetrical diester whose formula may be represented by



$$\mathrm{H_5C_2O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CH_2{-}\underset{\underset{\displaystyle HO}{|}}{CH}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OC_2H_5}$$

The alkaline hydrolysis of this diester can be represented schematically by the four-step process given in Scheme I.

**Scheme I**



represent diester, two different monoesters, and the diion, respectively.

After a mathematical analysis of the above kinetic process was made, a study of the alkaline hydrolysis of diethyl malate was carried out in various dioxane–water media at several temperatures in order: (a) to demonstrate the validity of a four-step kinetic process for a reaction involving an unsymmetrical difunctional molecule, (b) to study the effect of the hydroxyl group in diethyl malate in the alkaline hydrolysis of this diester, (c) to relate each of the four rate constants to a mechanistic rationalization of the reaction, and (d) to improve and extend computer techniques as applied to reactions involving multifunctional compounds.

## Mathematical Analysis

The reactions to be considered are

$$\mathrm{A + B \xrightarrow{k_1} C + M}$$

$$\mathrm{A + B \xrightarrow{k_2} E + M}$$

$$\mathrm{A + C \xrightarrow{k_3} P + M}$$

$$\mathrm{A + E \xrightarrow{k_4} P + M}$$

where A, B, C, E, P, and M are hydroxide ion, diester, first monoester ion, second monoester ion, diion and ethanol, respectively. The pertinent rate equations for the above steps in terms of the molar concentrations, $A$, $B$, $C$, and $E$, are

$$-\frac{\mathrm{d}A}{\mathrm{d}t} = (k_1 + k_2)AB + k_3AC + k_4AE \qquad (1)$$

$$-\frac{\mathrm{d}B}{\mathrm{d}t} = (k_1 + k_2)AB \qquad (2)$$

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = -k_1AB + k_3AC \qquad (3)$$

$$-\frac{\mathrm{d}E}{\mathrm{d}t} = -k_2AB + k_4AE \qquad (4)$$

If one defines a new variable $\lambda$ as

$$\lambda = \int_0^t A\mathrm{d}t \qquad (5)$$

It follows that

$$\mathrm{d}\lambda = A\mathrm{d}t \qquad (6)$$

On substituting eq 6 into eq 1 through eq 4, one obtains four new differential equations which can be integrated. Constants of integration are evaluated in each case by use of the appropriate boundary conditions which are: $\lambda = C = E = 0$, $A = A_0$, $B = B_0$, at $t = 0$. The results of the integrations are given by eq 7–11.

$$B = B_0e^{-(k_1 + k_2)\lambda} \qquad (7)$$

$$C = \frac{k_1B_0}{(k_3 - k_1 - k_2)}[e^{-(k_1 + k_2)\lambda} - e^{-k_3\lambda}] \qquad (8)$$

$$E = \frac{k_2B_0}{(k_4 - k_1 - k_2)}[e^{-(k_1 + k_2)\lambda} - e^{-k_4\lambda}] \qquad (9)$$

$$P = B_0 - B - C - E \qquad (10)$$

$$A = A_0 + 2(B - B_0) + C + E \qquad (11)$$

Equation 11 can be rewritten as eq 12, namely

$$\beta = G_1e^{-S_1\lambda} + G_2e^{-S_2\lambda} + G_3e^{-S_3\lambda} = \sum_{i=1}^{3} G_ie^{-S_i\lambda} \qquad (12)$$

where

$$S_1 = k_1 + k_2 \qquad (13)$$

$$S_2 = k_3 \qquad (14)$$

$$S_3 = k_4 \qquad (15)$$

$$\beta \equiv \frac{(A - A_0)}{B_0} + 2 \qquad (16)$$

$$G_1 = 2 + \frac{k_1}{k_3 - S_1} + \frac{k_2}{k_4 - S_1} \qquad (17)$$

$$G_2 = \frac{-k_1}{k_3 - S_1} \qquad (18)$$

$$G_3 = \frac{-k_2}{k_4 - S_1} \qquad (19)$$

A procedure for evaluating the rate constants $k_1$, $k_2$, $k_3$, and $k_4$ through the direct use of eq 12 has been described under method 1, ref 2c. It is based upon first estimates of the $k$'s, expansion of eq 12 about first estimates *via* Taylor's expansion, least-squares solution for the correction terms to the first estimates, and repetition of the process using the corrected $k$'s as the new first estimates. However, the selection of the four initial estimates is quite important since the radius of convergence[3] is small. Our criteria of success were based both on convergence to final values and on obtaining good agreement between the experimental time–concentration curve and the calculated time–concentration curve which was obtained through use of eq 12 using the converged values of the rate constants.

## Materials and Apparatus

**DL-Diethyl Malate.** The ester was prepared from the acid according to a method in the literature.[4] The ester was vacuum

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[3] The radius of convergence is the range within which the initially estimated constants must lie in order to give convergence to the final values.

[4] E. Fischer and A. Speier, *Ber.*, 28, 3252 (1895).

distilled several times, the center cut being saved. The saponification equivalent indicated a purity of 100 ± 0.1%. A chromatographic analysis yielded one maximum only.

**Other Details.** The apparatus, procedure, and other pertinent factors have already been described.[2] Starting concentrations of the diester and of the sodium hydroxide were adjusted so that equivalent amounts were used (*i.e.*, $A_0 = 2B_0$, where $A_0$ and $B_0$ were the concentrations in moles/liter of hydroxide and diester, respectively). This restriction is not a necessity in the treatment presented in this paper but is merely a convenience.

## Calculations and Discussion

**Computing Program.** A program was designed which, with the exception of the reaction involving a tetrafunctional unsymmetrical molecule, permitted one to solve competitive-consecutive second-order processes involving mono-, di-, tri-, and tetrafunctional symmetrical and unsymmetrical molecules. Details will not be given here. However, one of the subroutines is an integration subroutine which transforms $\alpha$-time data ($\alpha = A/A_0$) into $\lambda$ data ($\lambda = \int_0^t A dt$). Since this becomes a critical derived set of data, we show in Table I a set of test data used to check our integration subroutine. The test data were derived using an exponential function which resembled the kinetic runs. Reference to the third and fourth columns of Table I shows good agreement between $\lambda_{\text{calcd}}$ and $\lambda_{\text{true}}$.

**Table I.** Evaluation of the Integration Subroutine

| Time, min | $\alpha$ | $\lambda_{\text{calcd}}$ | $\lambda_{\text{true}}$ |
|---|---|---|---|
| 4.00 | 0.6994 | 0.03359 | 0.03364 |
| 6.00 | 0.5881 | 0.04643 | 0.04648 |
| 8.00 | 0.4967 | 0.05725 | 0.05729 |
| 10.00 | 0.4216 | 0.06641 | 0.06645 |
| 12.00 | 0.3598 | 0.07420 | 0.07425 |
| 14.00 | 0.3089 | 0.08088 | 0.08092 |
| 16.00 | 0.2669 | 0.08662 | 0.08666 |
| 18.00 | 0.2323 | 0.09160 | 0.09164 |
| 20.00 | 0.2037 | 0.09595 | 0.09599 |
| 22.00 | 0.1800 | 0.09977 | 0.09982 |
| 24.00 | 0.1603 | 0.10317 | 0.10322 |
| 26.00 | 0.1440 | 0.10621 | 0.10626 |
| 28.00 | 0.1303 | 0.10895 | 0.10899 |
| 30.00 | 0.1189 | 0.11144 | 0.11148 |
| 35.00 | 0.0976 | 0.11681 | 0.11686 |
| 40.00 | 0.0835 | 0.12132 | 0.12137 |
| 55.00 | 0.0614 | 0.13194 | 0.13198 |
| 65.00 | 0.0536 | 0.13766 | 0.13769 |

**Evaluation of Rate Constants.** Time–concentration data involving a primary run and its duplicate run for the hydrolysis of diethyl malate in 30 wt % dioxane–water mixtures at 15° are listed in the first two columns of Table II. The values of $\lambda$ in column 3 were calculated from the time–concentration data using our integration subroutine. The values of $\beta_{\text{exptl}}$ in column 5 were calculated by use of eq 16. Column 6 lists the values of $\beta_{\text{calcd}}$ obtained by use of eq 12 using the rate constants evaluated from the experimental data. Column 7 lists the per cent difference between $\beta_{\text{exptl}}$ and $\beta_{\text{calcd}}$, and this is a measure of the reliability of the rate constants over the whole concentration range. The standard deviation of the concentrations about the fitted curve (*i.e.*, the quadratic mean error of fit) is defined by

$$\text{QME} = \left[\frac{\sum(\beta_{\text{exptl}} - \beta_{\text{calcd}})^2}{n - 4}\right]^{1/2} \tag{20}$$

where $n$ is the number of data points and 4 is the number of parameters (*i.e.*, the number of rate constants) being varied. The error of a rate constant is defined by

$$\text{Err}(k_j) = (\text{QME})|\text{wt}_j|^{1/2} \tag{21}$$

where $k_j$ is the particular rate constant under consideration, and $\text{wt}_j$ is the least-squares weight, which is the reciprocal of the variance squared and is defined by the equation

$$\text{wt}_j = \frac{1}{\sum_n \left(\frac{\partial\beta}{\partial k_j}\right)^2} \tag{22}$$

The QME of fit and the expected error in the $k_j$'s are given in Table II for three cases: the primary run, the duplicate run, and the pooled data of both runs. Table III summarizes the rate constants obtained in this research under various environmental conditions.

**Comments on Errors.** Reference to Tables II and III will show the statistically calculated errors in the $k$'s. The most important error is the computational error introduced by the graphical integration. Reference to Table I shows that the integration procedure is accurate as long as the data points are sufficiently close together *over the whole concentration range*. However, as reference to Table II will show, the reaction was nearly 43% completed at the time of the first sample in the primary run, and nearly 36% completed at the time of the first sample in the duplicate run. If one calculates $\lambda$ values for the primary run, for the duplicate run, and for the pooled data of both runs, one observes a variation of about 3% between the first $\lambda$ values as obtained from the primary run data and from the pooled data and about 0.5% between the first $\lambda$ values as obtained from the duplicate run and from the pooled data. Now, if the results of the test data in Table I are any indication, the error in the first $\lambda$ value after 31% completion is less than two parts per thousand. However, in this latter case, one used data points sufficiently close together. In the actual experimental measurements, one is limited by the experimental procedures in obtaining a sample in less than about 1.5 min. We attribute the differences between the rate constants obtained from the data of the primary run and the data of the duplicate run to the error in the first integration interval. The rate constants calculated from the data of the pooled runs should be the most accurate. Actually we believe that the best criterion for the validity of the calculated rate constants is the QME of fit. These are listed for all of the runs in the last column of Table III and they varied from 0.15% to about 1% in the poorest case. Table II, column 7, shows the per cent difference between $\beta_{\text{exptl}}$ and $\beta_{\text{calcd}}$ for run 2 over the whole concentration range. The differences are rather small and in most places random.

Figure 1 shows the concentrations of the various species B, C, E, and P at various times for run 2 as calculated through use of eq 7, 8, 9, and 10, respectively.

**Mechanism.** To gain some insight into the reaction mechanism, the rate constants for the hydrolysis of diethyl malate should be compared with the rate constants for the hydrolysis of diethyl succinate[2e] under somewhat similar environmental conditions. Such results are tabulated in Table IV. Diethyl succinate, a symmetrical diester, differs from diethyl malate, an un-

**Table II.** Data in Dioxane–Water at 15.07°[a]

| Time, min | $\alpha$ (= $A/A_0$) | λ | Run[b] | $\beta_{\text{exptl}}$ | $\beta_{\text{calcd}}$ | % error |
|---|---|---|---|---|---|---|
| | | Run No. 2, Diethyl Malate (DL) | | | | |
| 0.00 | 1.0000 | 0.00000 | | 2.00000 | 2.00000 | 0.00 |
| 2.00 | 0.6441 | 0.01935 | D | 1.28829 | 1.29078 | −0.194 |
| 3.00 | 0.5778 | 0.02671 | P | 1.15566 | 1.16335 | −0.666 |
| 4.00 | 0.5427 | 0.03349 | D | 1.08530 | 1.08049 | 0.444 |
| 5.00 | 0.5150 | 0.03990 | P | 1.03002 | 1.02250 | 0.731 |
| 6.00 | 0.4919 | 0.04601 | D | 0.98381 | 0.97999 | 0.389 |
| 7.00 | 0.4739 | 0.05187 | P | 0.94788 | 0.94744 | 0.046 |
| 8.05 | 0.4605 | 0.05781 | D | 0.92099 | 0.92028 | 0.077 |
| 9.00 | 0.4498 | 0.06306 | P | 0.89956 | 0.89996 | −0.045 |
| 11.00 | 0.4317 | 0.07375 | P | 0.86331 | 0.86500 | −0.288 |
| 12.00 | 0.4242 | 0.07894 | D | 0.84849 | 0.85167 | −0.375 |
| 13.00 | 0.4196 | 0.08406 | P | 0.83915 | 0.83887 | 0.034 |
| 14.00 | 0.4122 | 0.08911 | D | 0.82433 | 0.82713 | −0.340 |
| 16.00 | 0.4025 | 0.09899 | D | 0.80500 | 0.80611 | −0.139 |
| 17.00 | 0.3978 | 0.10384 | P | 0.79566 | 0.79653 | −0.109 |
| 22.00 | 0.3771 | 0.12733 | D | 0.75425 | 0.75513 | −0.116 |
| 25.00 | 0.3676 | 0.14088 | P | 0.73526 | 0.73400 | 0.172 |
| 30.00 | 0.3518 | 0.16270 | D | 0.70350 | 0.70315 | 0.050 |
| 35.00 | 0.3386 | 0.18364 | P | 0.67728 | 0.67656 | 0.106 |
| 40.00 | 0.3264 | 0.20381 | D | 0.65276 | 0.65326 | −0.077 |
| 45.00 | 0.3169 | 0.22332 | P | 0.63379 | 0.63256 | 0.193 |
| 50.00 | 0.3070 | 0.24224 | D | 0.61410 | 0.61397 | 0.020 |
| 55.00 | 0.3000 | 0.26066 | P | 0.59996 | 0.59711 | 0.475 |
| 70.00 | 0.2768 | 0.31304 | D | 0.55368 | 0.55451 | −0.149 |
| 75.00 | 0.2734 | 0.32973 | P | 0.54681 | 0.54230 | 0.825 |
| 95.00 | 0.2480 | 0.39310 | P | 0.49607 | 0.50047 | −0.887 |
| 115.00 | 0.2323 | 0.45128 | P | 0.46466 | 0.46693 | −0.488 |
| 140.00 | 0.2154 | 0.51914 | P | 0.43084 | 0.43207 | −0.285 |
| 190.00 | 0.1888 | 0.64134 | P | 0.37768 | 0.37759 | 0.026 |
| 220.00 | 0.1768 | 0.70781 | P | 0.35352 | 0.35139 | 0.602 |

Primary Run; Quadratic Mean Error of Fit = 0.315%

| | | | |
|---|---|---|---|
| $k_1$ | 42.86 ± 0.80 | $k_3$ | 1.06 ± 0.04 |
| $k_2$ | 15.73 ± 0.92 | $k_4$ | 8.57 ± 0.50 |

Duplicate Run; Quadratic Mean Error of Fit = 0.226%

| | | | |
|---|---|---|---|
| $k_1$ | 44.60 ± 3.0 | $k_3$ | 1.13 ± 0.18 |
| $k_2$ | 14.69 ± 3.2 | $k_4$ | 9.32 ± 1.46 |

Combined Run; Quadratic Mean Error of Fit = 0.311%

| | | | |
|---|---|---|---|
| $k_1$ | 43.71 ± 0.67 | $k_3$ | 1.06 ± 0.03 |
| $k_2$ | 16.13 ± 0.75 | $k_4$ | 8.62 ± 0.38 |

[a] $D = 54.74$; $A_0 = 0.012136\ M$; $B_0 = {}^1\!/_2 A_0$; wt % of dioxane = 30.0. [b] D = duplicate; P = primary.

symmetrical diester, essentially only by the absence of a hydroxyl group on the $\alpha$ carbon. Consequently, any variation in the rate constants of the hydrolysis reactions involving these two diesters must be attributed to effects due to the presence of the hydroxyl group. Since the ester groups of diethyl succinate are mathematically indistinguishable, the values of $k_{1\text{S}}$ and $k_{2\text{S}}$ listed in Table IV are equivalent to the sums ($k_{1\text{u}}' + k_{2\text{u}}'$) and ($k_{3\text{u}}' + k_{4\text{u}}'$), respectively, in which notation they are now comparable to the four rate constants of the kinetically equivalent diethyl malate reaction. The last column of Table IV shows the ratios by which the rate constants of the diethyl malate hydrolysis reaction are larger than those of the diethyl succinate reaction. If one uses the Taft substituent constants[5] for the methyl and hydroxymethyl groups (0 and 0.56, respectively) and the Taft reaction constant[5] for the basic hydrolysis of esters (2.48), it may be calculated that an $\alpha$-hydroxy substituent should increase the rate of basic hydrolysis of an ester by 25-fold. The increases reported in Table IV for $k_1$ and $k_4$ are 17- and 26.5-fold, respectively. Accepting a falloff factor of 2.8-fold per carbon, similar calculations show that a $\beta$-hydroxy substituent should increase the reactivity by about 3.1-fold. The increases reported in Table IV for $k_2$ and $k_3$

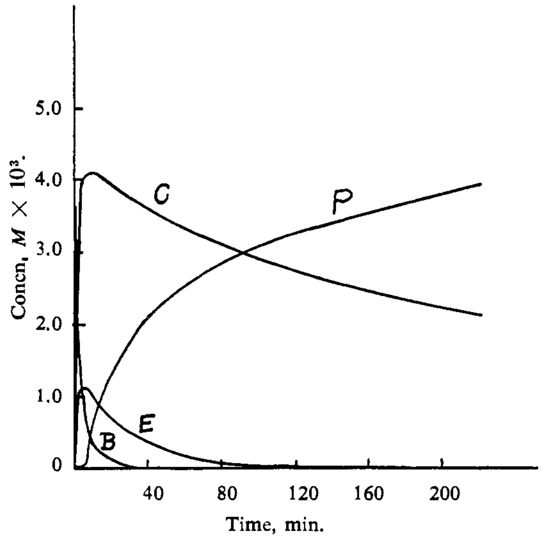

Figure 1. Plot of ester and intermediates *vs.* time.

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(5) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 96–97.

Table III. Summary of Rate Constants

| Run | Temp, °C | Dioxane, wt % | $D$ | $A_0$, $M$ | $k_1$, l./mole min | $k_2$, l./mole min | $k_3$, l./mole min | $k_4$, l./mole min | QME, % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 15.07 | 20 | 63.97 | 0.01203 | 42.8 ± 0.9 | 11.5 ± 1.0 | 1.28 ± 0.05 | 9.5 ± 0.7 | 0.151 |
| 2 | 15.07 | 30 | 54.74 | 0.01214 | 43.7 ± 0.7 | 16.1 ± 0.7 | 1.06 ± 0.03 | 8.6 ± 0.4 | 0.311 |
| 3 | 15.07 | 50 | 36.25 | 0.01228 | 44.9 ± 2.2 | 19.6 ± 2.3 | 0.99 ± 0.10 | 8.0 ± 0.8 | 0.611 |
| 4 | 15.07 | 70 | 18.71 | 0.01232 | 47.8 ± 1.1 | 25.5 ± 1.3 | 2.68 ± 0.11 | 20.4 ± 1.1 | 0.476 |
| 6 | 24.94 | 30 | 51.92 | 0.01203 | 77.4 ± 2.0 | 32.2 ± 2.2 | 1.95 ± 0.11 | 16.4 ± 1.0 | 0.342 |
| 7 | 24.94 | 70 | 17.70 | 0.01220 | 87.6 ± 1.0 | 48.6 ± 1.3 | 5.55 ± 0.09 | 38.8 ± 1.1 | 0.264 |
| 8 | 34.27 | 30 | 49.18 | 0.01192 | 120.8 ± 1.5 | 46.5 ± 1.8 | 3.45 ± 0.09 | 29.5 ± 1.1 | 0.263 |
| 9 | 5.05 | 30 | 57.77 | 0.01219 | 18.5 ± 6.2 | 13.7 ± 6.4 | 0.35 ± 0.31 | 3.2 ± 1.1 | 1.172 |
| 10 | 5.05 | 70 | 19.80 | 0.01245 | 19.3 ± 2.0 | 20.0 ± 2.2 | 0.94 ± 0.18 | 7.1 ± 0.7 | 0.942 |
| 11[a] | 15.07 | 70 | 18.71 | 0.01232 | 46.4 ± 0.7 | 24.7 ± 0.9 | 3.21 ± 0.10 | 25.5 ± 1.0 | 0.152 |
| 12[b] | 15.07 | 70 | 18.71 | 0.01129 | 16.0 ± 6.1 | 34.0 ± 6.6 | 0.47 ± 1.6 | 13.9 ± 2.3 | 0.500 |

[a] KI added = 0.02 *M*. [b] KI added = 1.830 *M*.

Table IV. Rate Constants for the Basic Hydrolysis of the Diethyl Malate and Diethyl Succinate Reactions

| Diethyl malate | Diethyl succinate | Ratio of $k_i/k_i'$ |
|---|---|---|
| $k_1 = 42.85$ | $k_{1S} = 5.03$, $k_{1u}' = 2.52$ | 17.0 |
| $_2$ 11.51 | $k_{2u}' = 2.52$ | 4.6 |
| 1.28 | $k_{2S} = 0.717$, $k_{3u}' = 0.36$ | 3.6 |
| 9.55 | $k_{4u}' = 0.36$ | 26.5 |

are 4.6- and 3.6-fold, respectively. Thus it appears that a hydroxy substituent has about the influence in the rate constant that would be expected from its inductive effect.[6]

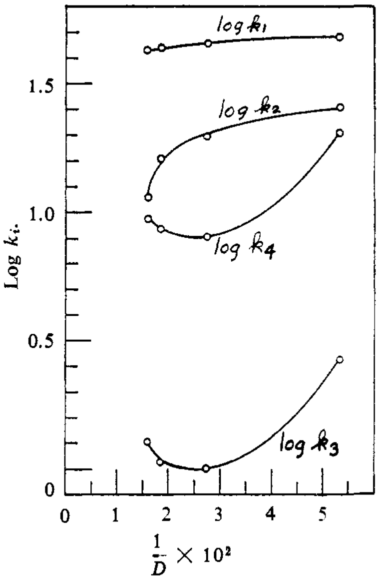

Figure 2.

**Thermodynamic Activation Terms and Medium Effects.** Activation energies and the Arrhenius frequency factors for the malate reaction were calculated through use of the least-squares method applied to the linear form of the Arrhenius equation, namely

$$\log k = \log A - \frac{E}{2.303RT} \qquad (23)$$

The free energies and the entropies of activation at 25° were calculated through use of the usual equations, namely

$$\Delta F^{\ddagger} = 2.303RT\left(\log \frac{RT}{Nh} - \log k\right) \qquad (24)$$

$$\Delta S^{\ddagger} = 2.303R \log A - \log \frac{eRT}{Nh} \qquad (25)$$

Data obtained in the temperature range of 15 to 34° only were used. The calculations are summarized in Table V. In an Arrhenius plot, the data obtained at 5° deviate considerably from the linear plot obtained in the above temperature range. It is possible that at 5°, a temperature not far from the freezing points of the two components in the solution, structural order in the solvent may be responsible for the variation observed above.

Table V. Thermodynamic Activation Quantities (24.94°) for the Diethyl Malate Reaction[a]

| | Wt % dioxane | |
|---|---|---|
| | 30 | 70 |
| $E_1$, kcal/mole | 9.34 | 10.49 |
| $E_2$, kcal/mole | 9.75 | 11.17 |
| $E_3$, kcal/mole | 10.81 | 12.59 |
| $E_4$, kcal/mole | 11.28 | 11.16 |
| $\Delta F^{\ddagger}_1$, kcal/mole | 14.87 | 14.80 |
| $\Delta F^{\ddagger}_2$, kcal/mole | 15.39 | 15.15 |
| $\Delta F^{\ddagger}_3$, kcal/mole | 17.05 | 16.44 |
| $\Delta F^{\ddagger}_4$, kcal/mole | 15.79 | 15.28 |
| $\Delta S^{\ddagger}_1$, eu | −20.61 | −16.44 |
| $\Delta S^{\ddagger}_2$, eu | −21.11 | −15.35 |
| $\Delta S^{\ddagger}_3$, eu | −22.93 | −14.88 |
| $\Delta S^{\ddagger}_4$, eu | −17.13 | −15.81 |
| Log $A_1$ | 8.723 | 9.634 |
| Log $A_2$ | 8.615 | 9.873 |
| Log $A_3$ | 8.216 | 9.975 |
| Log $A_4$ | 9.484 | 9.773 |

[a] Data in the temperature range of 15 to 34° were used for the calculations.

The variation in the log $k_i$'s with dielectric constant is shown by Figure 2. If one compares the behavior of the log $k_1$ and log $k_2$ curves of the diethyl malate reaction with the behavior of the log $k_1$ curves of the diethyl malonate, diethyl succinate, and diethyl sebacate reactions,[2e] one observes completely reversed behavior; *i.e.*, in the case of the diethyl malate reaction, the rate constants for the steps involving the saponification of the first ester group increase with decrease in the dielectric constant. However, the log $k_3$ and log $k_4$ curves of the

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[6] We wish to express our appreciation to an anonymous referee for the above argument.

malate reaction go through a minimum at about $D = 30$, similarly to the results observed in the three symmetrical diesters for the saponification of the second ester group.

**Salt Effects.** Runs 11 and 12 Table III were carried out under similar environmental conditions as in run 4 except for the addition of an inert electrolyte. On comparing the results of runs 4 and 11 it is observed that there is an appreciable positive primary salt effect on the rate constants $k_3$ and $k_4$ when a small quantity of an inert electrolyte is used. However, on using large quantities of an inert electrolyte, a large negative primary salt effect in the rate constants $k_3$ and $k_4$ is observed (see runs 4 and 12). Such complete reversal of primary salt effects is compatible with the behavior of the activity coefficients of an ion as one goes from a solution of low ionic strength to a solution of high ionic strength. It emphasizes the hazards of mechanistic interpretation of reactions in solutions which are highly swamped with an inert electrolyte, a practice which is all too common.

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# *ortho*-Substituent Effects in Polarography[1a]

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**Abstract:** A series of substituted bromo- and iodobenzenes were polarographically reduced to investigate the *ortho* effect. It was found that the *ortho* effect could be interpreted as the result of two phenomena: (1) that the inductive effect of an *ortho* substituent is proportional to, but greater than, the inductive effect of that substituent in the *para* position; (2) that the resonance interaction of a substituent is hindered when it is adjacent to a bulky group such as the halides. Using these principles, the *ortho* half-wave potentials were correlated with the *meta* and *para* half-wave potentials and the Hammett function.

A number of studies have been performed to determine the effect of substituent groups on the electrochemical reduction of aromatic compounds. In many cases it has been noted that *ortho*-substituted compounds are much easier to reduce than would have been predicted. For example, the half-wave potential of a reducible aromatic compound is almost always lower for the *ortho*-substituted compound than for the *meta* or *para* isomers. Furthermore, many electron-donating groups aid, rather than hinder, reduction when they are placed in the *ortho* position. The abnormal polarographic behavior has been termed the "*ortho* effect."

These low half-wave potentials were first observed for compounds such as *o*-hydroxybenzaldehyde[2] and *o*-nitrophenol[3] and were attributed to hydrogen bonding. However, the *ortho* effect was subsequently observed to be a rather general phenomenon, often occuring in cases such as the reduction of *o*-chloroiodobenzene,[4] where there are no hydrogens involved. A recent review[5] points out the wide occurrence of marked positive shifts in cases where hydrogen bonding is unacceptable as an explanation, and states that the contribution of the formation of hydrogen bonds to the shift of half-wave potential cannot be taken as proven in any case so far reported.

This same review notes that *ortho* enhancement of reduction is a fairly consistent phenomenon in various systems, but no explanation of this effect is offered. For the most part, quantitative studies have concentrated on compounds with substituents in the *meta* and *para* positions and avoided the problems of the *ortho* case. We believe that the *ortho* effect can be explained as a change in the electron density at the reaction site due to a decrease in the resonance contribution and an increase in the inductive contribution for a substituent in the *ortho* position. Since no previous experimental work had been specifically concerned with *ortho* compounds, it was necessary that a reaction series be thoroughly investigated under controlled conditions to properly evaluate these effects. The phenyl halides were studied because their reaction is not sensitive to pH.[6]

## Experimental Section

**Instrumentation.** Polarograms were obtained using an operational amplifier polarograph similar in design to that of Kelley,

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(1) (a) Presented in part at the 127th Meeting of the Electrochemical Society, San Francisco, Calif., May 1965. This article is based on a thesis submitted by W. W. Hussey in partial requirement for the Ph.D. degree to Lehigh University, June 1965. (b) National Science Foundation Graduate Fellow, 1963-1965. (c) Person to whom correspondence should be addressed.

(2) G. Semerano and V. Capitanio, *Gazz. Chim. Ital.*, 70, 490 (1940).

(3) M. J. Astle and W. V. McConnel, *J. Am. Chem. Soc.*, **65**, 35 (1943).

(4) E. L. Colichman and S. K. Liu, *ibid.*, **76**, 913 (1954).

(5) P. Zuman, *Collection Czech. Chem. Commun.*, **27**, 648 (1962).

(6) P. J. Elving and C. S. Tang, *J. Am. Chem. Soc.*, **74**, 6109 (1952).