

Kinetics of the Saponification of Diethyl Adipate

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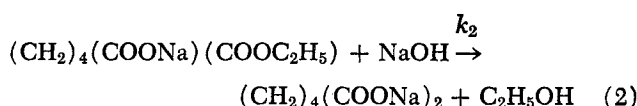
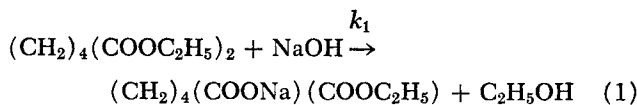
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Much of chemical reaction engineering theory depends upon the existence of real reaction systems which possess simple order rate laws—first-order irreversible, second-order reversible, etc. However, the experimentalist faced with the necessity of obtaining accurate kinetic data for the implementation of such theory often finds it difficult to find real systems for which such data exists. The intent of this note is to present such data for the case of a second-order, irreversible, consecutive homogeneous reaction in the liquid phase, namely, the saponification of diethyl adipate. A vital part of such an exposition is the analysis of the accuracy of the model parameters, the possible competing reactions, the interaction with other rate processes such as heat and mass transfer, and the analytical scheme.

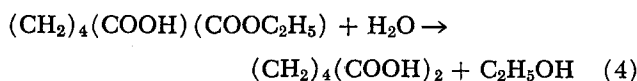
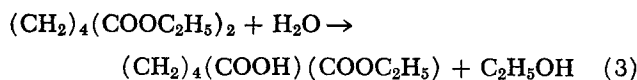
Ingold (1930, 1931), Frost and Schwemer (1952), and Westheimer et al. (1942) give experimental values of the rate constants for the saponification of diethyl adipate. These authors studied many diesters at a single temperature to obtain the effects of various substituents on reaction rates and in particular the rate constants for the saponification of diethyl adipate with sodium hydroxide. The results of these investigations are shown in Table 1. For comparison, extrapolated values at 293.1 K from this study are also given.

STOICHIOMETRY

The chemical reactions of interest are



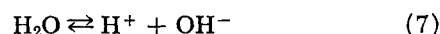
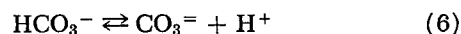
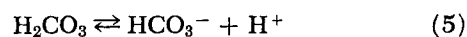
The reactions are irreversible in alkaline solution due to the stabilizing effect caused by resonance of the carboxyl ion, as discussed by Geissman (1959). It is perhaps unfortunate that pure diester is rarely available. Rather, a small amount of hydrolysis can occur in the diester solution



The rate of the above reactions is not the concern of this work; however, supposedly pure diester can contain up to 10% monoacid and 1% diacid. Thus, although the gravimetric concentration of diester used as feed material agreed with the saponification equivalent to within 0.4% for this work, this is in general no guarantee that the

adipate is present as diester.

Since the caustic and adipate solutions used unavoidably are in contact with air, the question of the carbonate-bicarbonate system influence arises. These reactions are



Equilibrium data for the above reactions is given by Roques (1964). The effect of the presence of carbonate is treated under Error Analysis.

CHEMICAL ANALYSIS OF REACTION PRODUCTS

The reaction can be quenched by allowing reactor effluent to flow into weighed flasks containing known quantities of hydrochloric acid. This effectively removes hydroxyl ion. Subsequent reweighing and a previous density determination allowed direct calculation of sample volumes. The original hydroxyl ion concentration is also easily determined by back-titration with standard sodium hydroxide. The end point was calculated to occur near pH 7.3. Following the work of Frost and Schwemer (1952), bromthymol blue indicator having a color change from yellow to blue between pH 6.8 and 7.5 was used. Experimental titration curves using a pH meter verified the applicability of this indicator.

Ingold (1930, 1931) employed benzene and pentane to extract all unreacted ester from a mixture of diethyl adipate, monoethyl adipate, and adipate ion. His work showed that benzene extracts all the diester and a small fraction of monoester from aqueous solution. The least square fit of the data of this study gives

$$(C_R)_{\text{benzene phase}} = 0.0033 (C_R)_{\text{aqueous phase}} \quad (8)$$

After extraction of diester, the monoester concentration is determined by total saponification with excess NaOH followed by back-titration with standard HCl. After determining both hydroxyl ion and monoester concentrations, all other compositions may be calculated using an overall material balance.

REACTOR STUDIES

The saponification of diethyl adipate may be represented by the stoichiometric relations given in Equations (1) and (2). The course of these reactions has been found to be well represented by second-order rate laws.

In a batch isothermal system, mole balances yield the following differential equations:

$$\frac{dC_A}{dt} = -k_1 C_A C_B \quad (9)$$

$$\frac{dC_R}{dt} = (k_1 C_A - k_2 C_R) C_B \quad (10)$$

C_B , C_S , and C_E are more easily obtained by overall mate-

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TABLE 1. SUMMARY OF DETERMINATIONS OF RATE CONSTANTS FOR SAPONIFICATION OF DIETHYL ADIPATE WITH SODIUM HYDROXIDE

Investigator	Initial concentrations, kgmol/m ³			Temp., K	Rate constants, m ³ /kgmol · s	
	diester C _A	NaOH C _B	NaCl C _{NaCl}		k ₁	k ₂
Ingold (1930, 1931)	0.002	0.002	—	293.1	3.52	0.704
Frost and Schwemer* (1952)	0.01	0.01	0.2	298.1	5.20	1.83
Westheimer et al. (1942)	0.005-0.011	0.005-0.011	0.006-0.07	293.1	5.7-6.1	—
Westheimer et al. (1942)	0.01**	0.01-0.02	0.02-0.3	293.1	—	1.7-2.2
This study (extrapolated)	0.02	0.05	—	293.1	9.3	7.7

* Solvent was one part dioxane, three parts water.
** Sodium monoethyl adipate.

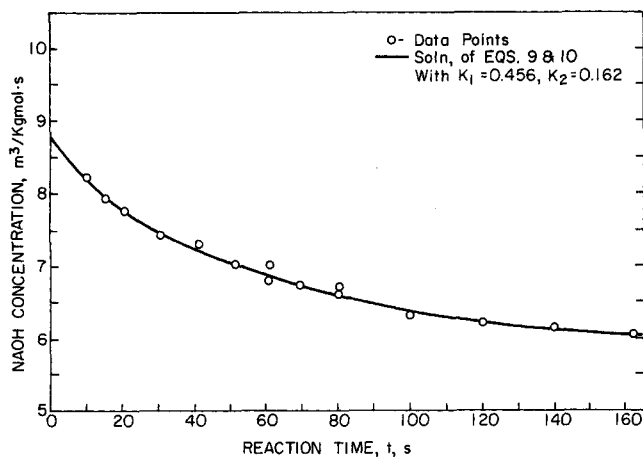


Fig. 1. Sodium hydroxide concentration profile for batch saponification at 319.2 K. Run No. 5.

rial balances. Because of the nonlinear character of the differential equations, no analytic solution is available for concentration-time profiles. We may thus view the problem of determining the reaction rate constants k_1 and k_2 as one in nonlinear regression. Given a set of concentration-time data, we may find the values k_1 and k_2 which best fit this data by repeatedly solving Equations (9) and (10) and employing a numerical search method to minimize

$$I_1 = \sum_{j=1}^N [C_{\text{exp}}(t_j) - C_{\text{calc}}(t_j)]^2 \quad (11)$$

Batch tests were made in stirred 50-ml Erlenmeyer flasks immersed in a constant temperature bath. The saponification reaction was initiated by pipetting the required volume of sodium hydroxide solution into the ester solution. After the required time, a known volume of hydrochloric acid was added to quench the reaction. Hydroxyl ion concentration was then determined by back-titration with standard sodium hydroxide solution.

Eight sets of batch runs were made between 302 K and 358 K. The maximum variations in temperature were ± 0.1 K. A typical concentration-time profile is shown in Figure 1. The data points on Figure 2 show the values of reaction rate constants and the range of probable errors in all measurements.

The tubular reactor was a 6.35-mm ($\frac{1}{4}$ in.) copper tube, 45-m (150 ft.) long. Separate control could be exercised over the heating rate in each of the shell sections. Details of construction, as well as feed system design and instrumentation, are available from Newberger (1967).

Mathematical modeling of tubular reactors is discussed

in most texts on chemical engineering kinetics, such as those of Levenspiel (1965) and Denbigh and Turner (1965). For the reactor used in this work, conditions are not uniform along the entire length so that proper equations must be written to describe mass and heat transfer, and chemical reaction as a function of distance. Comparisons of predicted concentration profiles with experimental data show that the plug flow model satisfactorily predicts performance for adiabatic as well as nonadiabatic operation.

The equations governing the operation of the experimental reactor are derived in Newberger (1967). In these balances, the following assumptions were made:

1. Axial diffusion may be neglected.
2. Conversion Y , temperature, and velocity are independent of radial position.
3. Overall density is a function of temperature only.

The mole balances are

$$\frac{dY_A}{dZ} = \alpha \rho^2 k_1 Y_A Y_B \quad (12)$$

$$\frac{dY_R}{dZ} = \alpha \rho^2 Y_B (k_1 Y_A - k_2 Y_R) \quad (13)$$

where

$$\alpha = \left[\frac{S}{G_{Ai}} \left(\frac{C_{Ai}}{\rho_i} \right) \right] \quad (14)$$

Energy balances for tube and shell fluids are

$$\frac{dT_t}{dZ} = \left(\frac{1}{W_t C_t} \right) \pi D_{to} U_o (T_s - T_t) + \alpha G_{Ao} Y_B \rho^2 \cdot [(-\Delta H_1) k_1 Y_A + (-\Delta H_2) k_2 Y_R] \quad (15)$$

$$\frac{dT_s}{dZ} = \left(\frac{\pi D_{to} U_o}{W_s C_s} \right) (T_t - T_s) \quad (16)$$

Activation energies and frequency factors were chosen such that the plug flow model gave the best fit of the experimental data. The best fit was the set of trajectories which minimized

$$I_2 = \sum_{j=1}^N \left[\left(\frac{C_{B\text{calc}} - C_{B\text{exp}}}{C_{B\text{exp}}} \right)^2 + \left(\frac{C_{R\text{calc}} - C_{R\text{exp}}}{C_{R\text{exp}}} \right)^2 \right] \quad (17)$$

Normalization is necessary here to give equal weight to C_B and C_R . The fit of the plug flow model to data of reactor run number 3 is shown in Figure 3. Reaction rate constants calculated using these estimates are shown as solid lines in Figure 2, which represent the equations

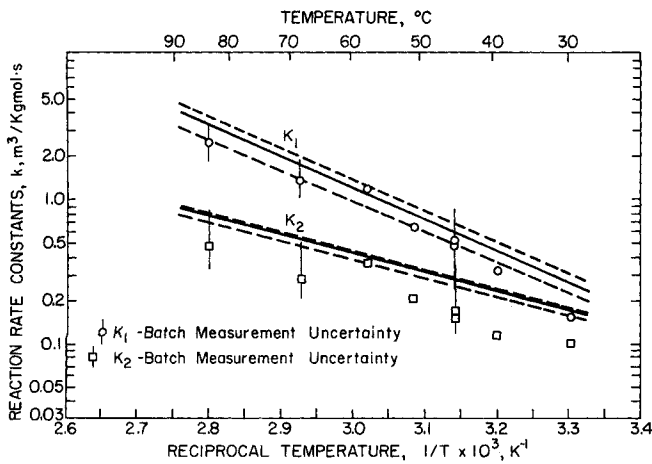


Fig. 2. Reaction rate constants for saponification of diethyl adipate with sodium hydroxide. Solid lines represent regression of tubular reactor Run No. 3. Dotted lines are uncertainty bands.

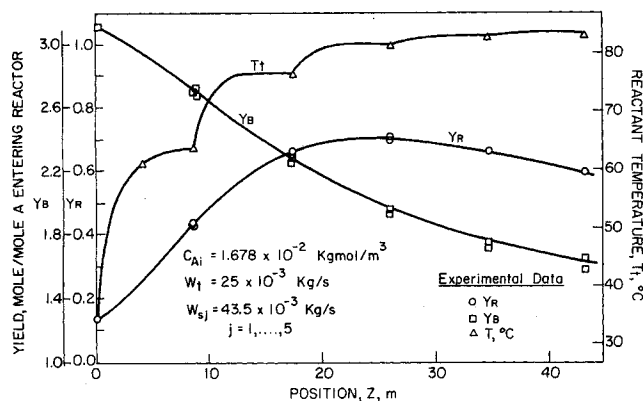


Fig. 3. Run No. 3 reactor concentration and temperature profiles. Lines represent plug flow model.

$$k_i = k_{i0} \exp(-E_i/RT) \quad i = 1, 2 \quad (18)$$

$$k_{10} = 4.87 \times 10^6 \text{ m}^3/\text{kgmol}\cdot\text{s}, \quad E_1 = 42.2 \text{ MJ/kgmol}$$

$$k_{20} = 3.49 \times 10^6 \text{ m}^3/\text{kgmol}\cdot\text{s}, \quad E_2 = 25.0 \text{ MJ/kgmol}$$

The numerical values in Equation (18) are those which fit the sodium hydroxide and monoethyl adipate data on tubular reactor run number 3. For the error analysis, all volumes and normalities used to calculate the experimental concentration profiles were perturbed by small amounts, and the profiles recalculated. The resulting activation energies and frequency factors yielded the rate constants denoted by the broken lines of Figure 2.

RELATED THERMODYNAMICS AND TRANSPORT PROCESSES

In addition to the rate constant determination discussed above, measurements and calculations were carried out to determine the heat transfer characteristics of the reactor, the heats of reaction, the axial dispersion coefficient, and the effect of radial gradients. The reader may obtain details of heat transfer and mixing from Newberger (1967). The heats of the two reactions were measured and found to be

$$\Delta H_1 = -45.2 \pm 3.4 \text{ MJ/kgmol}$$

$$\Delta H_2 = -68.0 \pm 4.2 \text{ MJ/kgmol}$$

These quantities contribute at most at 0.5 K temperature rise in the tubular reactor.

ERROR ANALYSIS

Although the diethyl adipate used in the kinetic experiments gave the proper saponification equivalent, it did not consist of pure diester. Approximately 10% was hydrolyzed to monoethyl adipic acid and a small amount of adipic acid. Measured values were used in all calculations. An investigation was made of the effect of changes in these initial conditions on the calculated values of k_1 and k_2 . An error in acidity of the ester solution of 0.001 kgmol/m³, which reduced the initial hydroxide concentration in the reaction mixture by 1% produced a 10% error in the regressed values of k_1 and k_2 . Furthermore, the effects of k_1 and k_2 were in opposite directions.

Carbon dioxide is absorbed by alkaline solutions. Carbonate, if unaccounted for, can introduce two different errors. In dilute solutions it hydrolyzes significantly as hydroxyl ion is consumed and acts as a buffering agent. A more serious error introduced by the presence of carbonate was its consumption of H^+ in acid solution. When sodium hydroxide is added to ester solution, saponification proceeds with carbonate acting essentially as an inert. When hydrochloric acid is added to quench the reaction, carbonate is transformed to carbonic acid which in turn dissociates to carbon dioxide and water, thus consuming acid. The solubility of carbon dioxide at room temperature and normal atmospheric conditions is only 5×10^{-5} kgmol/m³ so that most of the carbon dioxide which forms is evolved as gas. Hydroxyl ion concentration data for all batch runs were calculated taking into account the loss of acid due to evolution of carbon dioxide.

Error propagation in the hydroxyl ion concentration profile is far too serious to allow precise estimation of the rate constants by measuring only the exit hydroxyl ion concentration. This accounts for the significant difference between the batch data and tubular regression lines on Figure 2.

NOTATION

c	= heat capacity, J/kgmol·K
C	= concentration, kgmol/m ³
D	= diameter, m
E	= activation energies, J/kgmol
G	= molar rate, kgmol/s
I	= objective function
k	= reaction rate constant, m ³ /kgmol·s
k_{10}, k_{20}	= frequency factor in Arrhenius equation, m ³ /kgmol·s
N	= number of runs
R	= gas constant, 8314 J/kgmol·K
S	= cross-sectional area, m ²
t	= time
T	= temperature, K
U_o	= overall heat transfer coefficient, J/s·m ² ·K
W	= mass flow, kg/s
Y	= mole ratio, kgmol/(kgmol A entering reactor)
Z	= distance along reactor axis from inlet, m

Greek Letters

α	= defined in Equation (17)
$-\Delta H$	= heat of reaction, J/kgmol
ρ	= density, kg/m ³

Subscripts

A	= diethyl adipate, (CH ₂) ₄ (COOC ₂ H ₅) ₂
B	= sodium hydroxide, NaOH
E	= ethanol, C ₂ H ₅ OH
i	= initial or inside

- j* = counter
o = outside or feed condition
R = symbol for monoethyl adipate, $(\text{CH}_2)_4(\text{COONa})(\text{COOC}_2\text{H}_5)$
s = shell
S = adipate, $(\text{CH}_2)_4(\text{COONa})_2$
t = tube

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A Note on the Blasius Problem for Viscoelastic Fluids

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Denn (1967) considered the fundamental problem of boundary-layer flow over a semi-infinite flat plate with zero pressure gradient for a class of power-law viscoelastic fluids satisfying a constitutive relation of the Rivlin-Ericksen type. A perturbation about the inelastic flow was made by assuming a solution of the form

$$f(x, \eta) = f_0(\eta) + \epsilon x^{-s/n+1} f_1(\eta) + \text{higher order terms} \quad (1)$$

where n and s are the power-law exponents for shear-stress and normal-stress, respectively, and ϵ is an elastic parameter. Equation (1) may also be viewed as an inverse coordinate expansion valid for large x . The equations for f_0 and f_1 are found to be the following:

$$f_0''' + \frac{1}{n(n+1)} f_0 f_0''^{(2-n)} = 0 \quad (2)$$

$$\begin{aligned}
 f_1''' + \frac{2-n}{n(n+1)} f_0 f_0''^{(1-n)} f_1 \\
 + \frac{s}{n(n+1)} f_0' f_0''^{(1-n)} f_1' + \frac{1-s}{n(n+1)} f_0''^{(2-n)} f_1 \\
 = \frac{1}{n(n+1)} \left[\frac{s+1}{n(n+1)} f_0 f_0' f_0''^{(s+1-2n)} \right. \\
 \left. + \frac{n-s}{n^2(n+1)^2} f_0^3 f_0''^{(s+2-3n)} - (3-2s) f_0''^{(n+s-1)} \right] \quad (3)
 \end{aligned}$$

$$f_0(0) = f_0'(0) = 0; \quad f_0'(\infty) = 1 \quad (4)$$

$$f_1(0) = f_1'(0) = f_1'(\infty) = 0 \quad (5)$$

In these equations primes denote total derivatives. Denn obtained solutions for the cases ($n = 1, s = 2$) and ($n = 1, s = 1.5$) having values of $f_1''(0) = 0.03$ and -0.082 , respectively.

Lockett (1969) showed that in the special case of a second-order fluid ($n = 1, s = 2$) there exists an infinite number of solutions to Equation (3) satisfying the boundary conditions (5). The difficulty is due to an eigensolution of the classical Blasius problem of the form

$$f_1(\eta) = A[f_0(\eta) - \eta f_0'(\eta)] \quad (6)$$

which satisfies the homogeneous version of (3) for any value of the constant A . This eigensolution, which is the first of an infinite, discrete set (see, for example, Van Dyke, 1964b), was first encountered by Alden (1948) in connection with the third-order boundary-layer approximation for the flat plate.

The correct solution for the second-order fluid was given by Davis (1967) who showed that a logarithmic term occurs in the expansion for $f(x, \eta)$. Thus, (1) must be replaced by

$$\begin{aligned}
 f(x, \eta) = f_0(\eta) + \frac{\epsilon}{x} \left[\log \frac{x}{\epsilon} f_{11}(\eta) + f_{12}(\eta) \right] \\
 + \text{higher order terms} \quad (7)
 \end{aligned}$$

The solution for $f_{11}(\eta)$ is found to be the eigensolution (6) with the constant A determined by the condition of exponential decay of vorticity. However, as in the analogous problem of Newtonian boundary-layer flow far downstream on a parabola (Van Dyke, 1964a), a unique solution for $f_{12}(\eta)$ cannot be obtained due to the presence of the eigensolution.

Consider now the general case of arbitrary (positive)