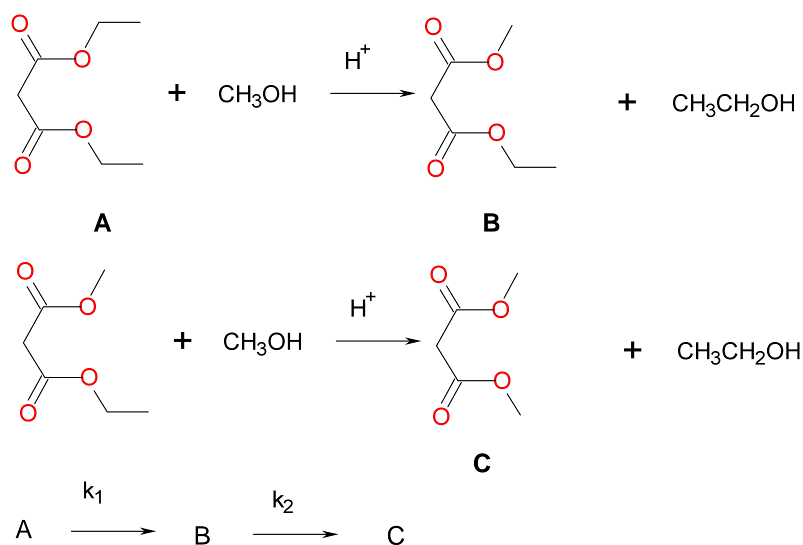
The Kinetics of the Methanolysis of diethyl malonate: determination of rate constants of a two step consecutive reaction.

Background:

Methanolysis of diethyl malonate to produce the dimethyl malonate effectively entails two successive steps. The kinetics of the reaction is such that it is functionally first order with respect to the diester and alcohol in both steps. In reality these reactions are much complicated, involving equilibrium processes and catalysis (acid). The complex rate law will be simplified by the use of a large excess of a reactant and drives the reaction largely to the right. Especially at the early stages of the reaction the system, the reaction behaves as a system of first order consecutive reactions, for all practical purposes. The reactions are carried out in excess of one of the reactants (methanol) and each reaction is effectively a (pseudo) first order reaction. Under these conditions the two consecutive reactions are;

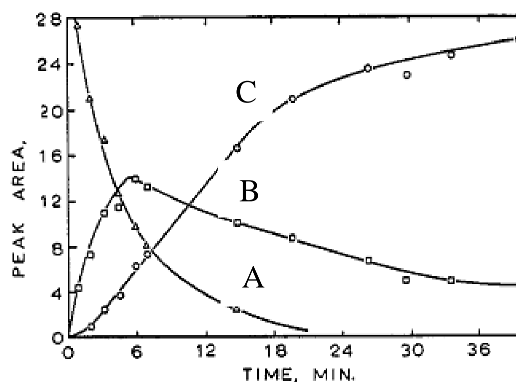


Concentration of acid, although affects the reaction rate, is held constant and factors into the rate constant of the rate equation, k_1 and k_2 are the reaction rate constants. The rate equations for the above system of reactions, upon integration yield the following.

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$[C] = [A]_0 \left(1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2}\right)$$



$[A]_o$ is the concentration of A at t=0. If the same response factor for A, B and C is assumed, the concentrations are proportional to the chromatographic peak heights (or more precisely peak areas). Kinetic data are obtained from changes of the peak dimensions, which are proportional to changes in concentration of the respective components in the mixture. All three peaks of interest are sufficiently sharp and therefore of the peak height is proportional to the concentration. All peak heights from a run must be normalized by taking ratios of peak heights to the sum of the peak heights.

Peak height or peak areas for each of the three esters are measured for each run. Peak areas for each of the three esters are measured for each run. The concentration of species in each form (A, B, and C) at a given time is proportional to the normalized areas. We are using the raw chromatographic signal (no internal standard used) and therefore areas were normalized.

$$[A]\ \alpha \frac{a_A}{a_A + a_B + a_C} \qquad [B]\ \alpha \frac{a_B}{a_A + a_B + a_C} \qquad [C]\ \alpha \frac{a_C}{a_A + a_B + a_C}$$

$$k_1 = \frac{2.303}{t} \log \frac{a_{A0} - a_{A\infty}}{a_{At} - a_{A\infty}} \cong \frac{2.303}{t} \log \frac{a_{A0}}{a_{At}}$$

$$\frac{[B]_{max}}{[A]_0} = \kappa^{\frac{\kappa}{1-\kappa}} \qquad \text{where } \kappa = \frac{k_2}{k_1} \text{ and } a_{it} = \text{peak area of species i at time t}$$

$$\text{Defining } a'_A \text{ as } \frac{a_A}{a_A + a_B + a_C} \text{ and upon rearrangement}$$

$$k_1 = \frac{2.303}{t} \log \frac{a'_{A0}}{a'_{At}} \Rightarrow \log a'_{At} = -\frac{k_1}{2.303} t + \log a'_{At}$$

Where, a_A, a_B, a_C, are the peak areas for components A, B, and C respectively. The response factors of A, B, and C are very close. Make kinetic plots; normalized peak height (a' = ratio of area to total of all areas, see above) vs. time for each of the three components. Normalization is necessary because the injection volumes can vary; [B] reaches a maximum value $[B]_{max}$ before dropping. Concentration of A drops from $[A]_0$ exponentially

The pseudo-first-order rate constant for the first step is then calculated from the (log a'_A) vs t curve by use of the relationship shown above, where k_1 is the pseudo-first-order rate constant, and $a'_{A,0}$, $a'_{A,\infty}$ infinity and $a'_{A,t}$ are the peak heights of A at reaction time equal 0, ∞ and t respectively. From the value of the slope the value for k_1 at a given acid concentration can be determined.

A value of the pseudo-first-order rate constant for the second step of the reaction, k_2, can be obtained by use of the relationship that expresses the maximum concentration of the intermediate B, to the original concentration of A. The ratio of $[B]_{max}/[A]_o$ is related to reaction rate ratio, κ, as given above. Solve for κ by successive approximation.

Apparatus: GC System:
column - 30-m x 0.32mm capillary with 0.25 μm coating of poly(14% cyanopropylphenyl/86% dimethyl) siloxane (Supelco Equity 1701), He carrier gas.
syringe - 1 uL, 50 mL 3-neck flask, thermostated bath, thermometer

Chemicals: methanol, diethyl malonate, conc. HCl, ammonia in methanol, dimethyl malonate and ethyl-methyl malonate (if available)

Procedure:

The analysis of the reaction mixture as function of time (for their relative concentrations) is carried out by isothermal GC analysis. Settings: injection port 220°C, inlet pressure 70 psi, column temperature 130°C, detector temperature 220°C.

I. (Optional) Run a trial to ascertain the time and order of elution of the components in the mixture. Prepare a sample that contains the available esters by mixing 1 ml each of the three esters in 6 mL methanol. Inject a 1-micoliter sample of the mixture into the column. Of the esters, dimethyl malonate (b.p. 199°C, density=1.055g/mL) elutes first, diethyl malonate last (b.p. 180-181 °C, density=1.154/mL), and ethyl-methyl malonate in between.

II. Prepare 10-15 vials containing 1.00mL of ammonia in methanol solution. Keep them capped.

Into a glass 100-mL 3-neck with flask directly dispense, using burettes, 18.00mL of methanol accurately, and 6.00mL of diethyl malonate. Shake the mixture and draw 50uL of the mixture into a vial prepared above, sample #0. Close the flask with stoppers. Obtain a chromatogram later to check the reagent purity (diethyl malonate may contain small amounts of both the ethyl-methyl and dimethyl ester). From their recorded peak areas, note the impurity peaks and if need be subtract these values from the peaks heights from the subsequent runs. Record the major peak areas (sans the solvent peak) regardless of the purity of the samples. Suggested injection volume is 1uL.

Stopper the reaction flask to prevent loss of methanol and place in a water bath maintained at 60° C. Note the actual temperature inside the flask (near 60°C). An aliquot of 600uL conc. HCl (catalyst) is then added; immediately start a stop watch (t =0) and keep the reaction vessel stirred and closed except for removal of samples for analysis at different reaction times. Withdraw volumes of 50uL and transfer immediately into a vial, already filled with 1mL of ammonia in methanol solution (of concentration 500uL ammonia/100mL methanol.) to arrest the reaction, at different reaction arrest times. Prepare many sample vials at various reaction arrest times (reaction time; t = 0 *to* the time of transfer *into* the vial) and chromatograph all the samples. Label vials in a systematic manner.

At the initial stages obtain sample vials of the reaction mixture at reaction time intervals of about 5min, later withdraw samples approximately in every 10-15 min intervals (note time of transfer accurately at all times).

Generate sample vials for about 2 – 2 1/2 hours, to generate as many data points as possible.

In your observations, note all parameters (column and operational): temperatures of column, detector and injector; column length, internal diameter, phases, etc.

Tabulate the results: suggested table.

time, t (sec)	a_A	a_B	a_C	a'_A	a'_B	a'_C

Treatment of Data:

Plot a'_A vs. time; a'_B vs. time; a'_C vs. time (overlay).

Generate a suitable (linear) plot of the variation of a'_A vs. time and by subsequent regression estimate the k_1 rate constant.

Calculate the 'second' rate constant by successive approximation (see below). Express the rate constants for the reaction temperature, conditions and use proper units.

Method of Successive Approximation to calculate the second rate constant - using a spreadsheet:

If κ is known one can calculate k_2 with k_1 already determined. But to find kappa we need k_2!!

The strategy is to use the *successive approximation technique*, where an initial ‘guess’ is made for kappa and this value is improved until the 'guess' equals the ‘best possible value’ for the given data set.

First step is to rearrange the expression for kappa shown above to;

$$\kappa = (1-\kappa)\frac{\log \frac{B_{max}}{A_0}}{\log \kappa} = f(\kappa) \quad \text{(say)}$$

If the correct value for kappa is guessed, the left hand side and the right hand side are equal. If not, change the left hand side value iteratively until they are equal. The strategy is to make the value of the right hand side calculated from an 'inaccurate initial” guess, the new “better initial guess” for kappa. Follow this procedure to improve the 'new' guess, until it converges to the correct value.

- enter the experimental value for B_{max}/A_0 (= appropriate a'- ratio) in cell (D4)
- enter an initial guess (say, 0.250) for kappa in cell (C8)
- enter the above formula in the adjacent cell (D8) referring to value in C8 for kappa.
- copy this cell down the column. D8..D25
- copy the cell D8 below the 'initial guess' for kappa i.e. C9
- copy the cell C9 down the column. C9..C25

kappa initial guess	RHS of preceding equation

Watch the convergence of the calculated value of κ. (For a graphical method, see Marasinghe P.A.B. et.al, J. Chem. Ed. 285, 69(4), 1992)

Reference:

David O. Johnston, A. B. Cottingharn, and W. Paul Roland, J.Am. Chem Soc., 244, 90(2), 1967