METHANOLYSIS OF ACETAL

1. Purpose

Diethyl acetal undergoes an acid-catalyzed reaction with methanol in two steps, as follows:

$$CH_3CH(OEt)_2 + MeOH \xrightarrow{k_1} CH_3CHOEtOMe + EtOH \qquad (I)$$

$$CH_3CHOEtOMe + MeOH \xrightarrow{k_2} CH_3CH(OMe)_2 + EtOH \qquad (II)$$

To study the kinetics of these reactions the concentrations of the various reagents (or products) have to be monitored as a function of time. For this purpose, two features of this system will be used: 1) all the compounds involved in reactions (I) and (II) are easily separated on a simple gas chromatograph (see Fig. 1), and 2) at any time the composition of the reacting mixture can be effectively frozen by addition of a base (ie, progress of reactions I and II can be stopped).

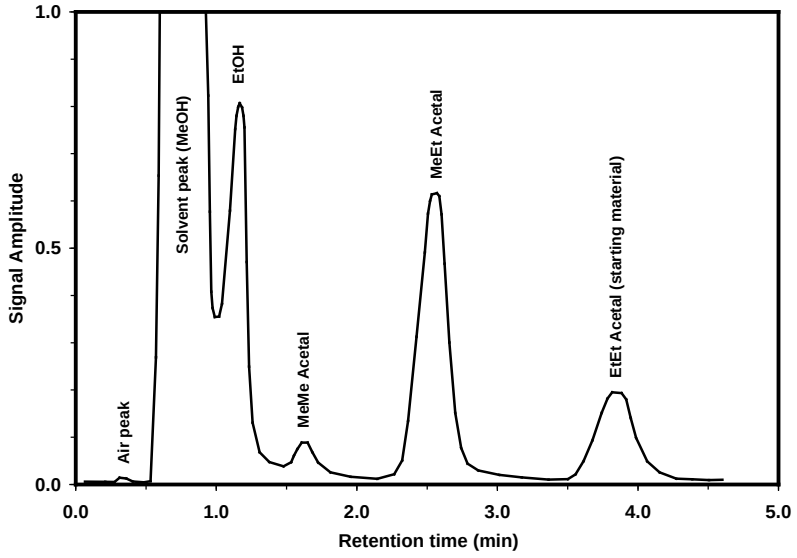

Fig. 1. Typical GC trace of the reaction mixture during the acid catalyzed methanolysis of diethyl acetal. Conditions: dioctyl phthalate on porapak column, 80C, ~45 ml/min He carrier gas.

Thus, the principle of the experiment is to withdraw at regular time intervals a small sample from the reaction mixture, stop the reactions in this

aliquot by addition of a small amount of conc. NH_3, then later subject the sample to GC analysis. Since the intensity (more precisely the surface area) of a GC peak is directly proportional to the amount of compound present, the concentration profile of the species present in the reacting mixture can be obtained by following the variation of the GC peak amplitude for each of the samples analyzed.

Both of the above reactions are really equilibria, having second-order kinetics in each direction. In this experiment, a large excess of methanol is used, which 1) forces the equilibria to the right, and 2) gives rise to pseudo-first-order kinetics; *ie,* instead of measuring the second order rate constants k_1 and k_2, one measures the pseudo-first rate constants $k_I = k_2[MeOH]$ and $k_{II} = k_2[MeOH]$ (why?) Thus, the system appears, kinetically, to behave like two consecutive first-order reactions with the various acetal molecules as reagents.

2. Safety

Wear eye protection at all times in the laboratory.

3. Procedure

The instructor will assign a reaction temperature (between 20 to 40 C) and acid catalyst concentration (between 1×10^{-4} to 5×10^{-4} M). You are provided with a 0.01 M solution of HCl in methanol. Dilute this accurately with dry methanol (the *Electronic grade* methanol is adequate) so as to obtain the assigned acid concentration *in the final 30 ml reaction mixture*.(consisting of 25 ml of the prepared acidified methanol and 5 ml of diethyl acetal – see below). If the methanol has been dried with molecular sieves, it must be filtered before use to remove particles, as molecular sieves particles will adsorb the catalyst HCl.

3.1 GC SET-UP

CAREFUL!! Do not turn on the filament current unless He is flowing through both columns. Never use more than 100 ma filament current. When finished, first switch off the detector power supply and then turn off the He tank gas supply; leave the column heater on.

- Gas carrier flow rate.
  Check that the helium flow rate into the dioctyl phthalate column of the gas chromatograph is about 40 to 50 ml per minute (≈12 - 15 s /10 ml).
- Injector and column temperature.
  Check that the temperature of the injector is > 100°C and that the column temperature is ~80°C; these parameters are not too critical but must remain the same for all the analyses. Ask the instructor to

verify that the injector septum has been changed since the GC was last used.

- Detector current.
  Use a filament current of 100 mA.
- The present GC set-up is fitted with two columns; the injection port corresponding to the dioctyl phthalate column is the *leftmost* port.
- Retention time and purity of starting material.
  Inject into the gas chromatograph a 1 – 2 μl aliquot of the acetal sample provided in order 1) to check the retention time of the starting material on the GC at hand, and 2) to check the purity of this particular batch; the presence of significantly intense peaks (other than the acetal peak) is an indication of an old sample of acetal, and should not be used for the experiment. The detector attenuation may need to be adjusted to optimize the signal sizes on the chart.
- Reproducibility.
  It is critical that the volume injected be the same (within errors) for all samples from the kinetic run. To check the reproducibility of your injections, practice by injecting a series of 2 μl samples of methanol and compare the peak height obtained; during this test the detector attenuation has to be adjusted to keep the methanol peak in scale.

3.2 EXPERIMENT AND SAMPLE COLLECTION

- Measure 25 ml of your prepared acid/MeOH solution and 5 ml of acetal into two separate 50 ml conical flasks.
- Place these into a thermostat bath at the assigned temperature.
- Leave the reagents to equilibrate in the bath for ≈ 15 min, start the reaction by mixing them thoroughly. Start the timer when the reagents are mixed. The reaction mixture stays in a capped flask immersed in the temperature bath throughout the experiment.
- At regular time interval[1] withdraw with a pasteur pipette a small volume (≈ 0.2 - 0.5 ml) from the reacting mixture and place it into a small pre-labeled vial, immediately quench the reaction in the vial by stirring with a glass rod which has just been dipped into concentrated NH_4OH solution. Record the time of quenching of each sample. Keep the sample vials tightly stoppered until analysis. No further reaction will take place after quenching, but if the vials are not properly stoppered evaporation is possible.

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[1] If the temperature assigned is less than 35 C, suitable sampling times are 1, 2, 3, 4, 6, 8 and 10 minutes, then every 5 minutes for at least one hour; if the assigned temperature is 35 C (or higher) sample twice as fast at the beginning.

- Once you are sampling at 5 minute intervals, you may start the GC analysis of samples already collected (see below).
- Keep sampling until you have observed on the GC signals that the peak corresponding to the methyl–ethyl acetal has gone through its maximum height. The best way to check for this is to analyze first the last sample collected, then the one before and compare the size of the MeEt peak between these two samples; you can stop sampling when you are sure that the size of the MeEt peak is decreasing with reaction time. Samples collected earlier can be analyzed at any time.

3.3 GC ANALYSIS

Analyze the collected samples by injecting a 5 μl aliquot; the detector gain has to be adjusted such that the various acetal peaks fill up as much as possible of the intensity scale on the chart paper, but keep the same gain setting for all your samples.

Make sure that the acetal (EtEt) peak has eluted trough the column before injecting the next sample.

4. Data Processing and Interpretation

Review the section on Chemical Kinetics in a Physical Chemistry textbook, in particular make sure you understand the concepts of first order, second order and pseudo-first order reactions.

Data are best handled with the help of a spreadsheet in combination with a weighted least squares.

First for each acetal peak, draw the appropriate baseline (line tangent to the bottom of the peak), then measure the height of the peaks relative to this baseline; a proper baseline is critical for the initially small di–methyl acetal signal (see Fig. 2). Generate a plot of these data. Reflect on the fact that by measuring only the height of the peaks (rather than the area), the effective response of the gas chromatograph for the different acetal species is not the same (see "Notes" below).

Next, analyze your data to obtain the pseudo-first-order rate constants for reactions I and II.

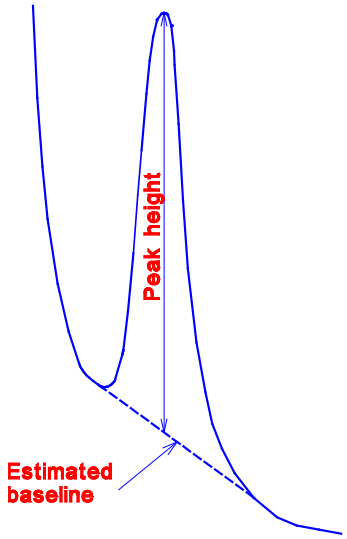

Fig. 2. Method to determine the "true" height of a GC peak located on the tail of another peak.

Standard analysis methods used for first-order reactions provide k_I (see ref. 1).

Several methods are suggested to obtain k_{II}:

a) by observing the time at which the concentration of methyl–ethyl acetal goes through a maximum as described in reference 1,

b) by making an analysis of the time variation of di–methyl acetal during steady-state (*i.e, the time range around which methyl–ethyl acetal goes through a maximum; since the maximum is rather flat, depending on the data, this time may be as long as ≈1/2 hour*). For this matter, during this "steady state" period only, the following approximation holds:

$$\frac{d[\mathrm{MeEt}]_t}{dt} \approx 0 \text{ ie, } [\mathrm{MeEt}]_t \approx [\mathrm{MeEt}]_{ss} \approx \text{constant}$$

Then show that a plot of $[\mathrm{MeMe}]_t$ versus time should be linear with slope = $k_{II}[\mathrm{MeEt}]_{ss}$., where $[\mathrm{MeEt}]_{ss}$ is the steady state concentration of MeEt.

c) by looking at the variation of the integral of the methyl–ethyl acetal as a function of the di–methyl acetal concentration. In this instance, show that a plot of

$$\sum_{i=0}^{t} [\mathrm{MeEt}]_i \times \Delta t_i \text{ versus } [\mathrm{MeMe}]_t$$

should be linear with slope $1/k_{II}$, where $[\mathrm{MeEt}]_i$ and $[\mathrm{MeMe}]_i$ represent acetal concentrations, *i*, the running index of successive

measurements and Δt_i the time interval between two consecutive samplings. Note that the data should be plotted in this manner because of the varying error on the sum. In your error analysis show that the error on the sum increases approximately as $i^{1/2}$.

d) by using the fitting program ACETAL.XLS[2] available in the PCHEM computers or from the course web site.

Compare the results obtained by the different procedures, but eventually report one value for each rate constant. From your analysis, discuss which method is expected to give the best value for k_{II}.

After obtaining the pseudo-first-order rate constants, work out the initial concentrations of reagents and calculate the corresponding second-order rate constants k_1 and k_2 for the forward reactions. Estimate how much error arises from treating this reaction as a pseudo first-order system. Discuss your experimental values in the context of the data tabulated in Ref. 1.

Notes on GC *peak height* versus *peak area*.

In Gas Chromatography (GC), the area of the GC peak is proportional to the concentration of a species. Therefore, by measuring peak areas, one can get the relative concentration of the various species present in the injected sample. However, the peak height is proportional to peak area *only* if the *peak width stays constant*, which is not the case for a GC injection as the width increases with increasing retention time (broadening of the peaks). Therefore, if one is to obtain accurate concentration information from the measurement of the height of the GC peaks, one has to generate a set of correction factors f_i (response constant) for each GC peak, which depends on retention time to take into account this broadening.

For species S_i one has:

$[S_i] \propto$ Peak Area(S_i) $\propto f_i$ x Peak Height(S_i)

In the present situation, only the values of the correction factors f_{MeEt} and f_{MeMe} *relative* to f_{EtEt} are needed (ie, one sets $f_{EtEt} = 1$). The spreadsheet ACETAL.XLS mentioned above will generate these relative response constants.

5. References

1. D.O. Johnston, *J. Chem. Educ.* **44**, 33 (1967)[3].

[2] Details on the principle of this fit can be found in Appendix IV.

[3] Photocopy of this article available in the course website.