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SAPONIFICATION OF SEVERAL ESTERS  
OF PILVALIC ACID

by

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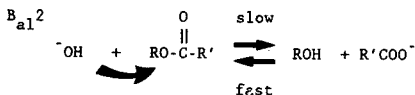
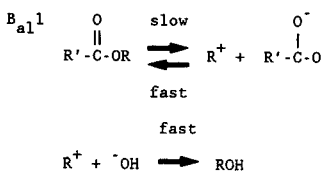
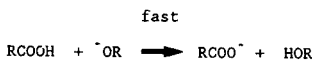
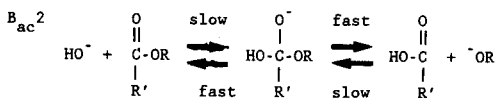
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## INTRODUCTION

The base promoted hydrolysis, saponification, of several esters of pivalic acid (trimethyl acetic acid -  $C(CH_3)_3COOH$ ) has been studied. Kinetic studies were performed and a possible mechanism for the reactions is proposed. The saponification of esters has been well studied. Ingold<sup>1</sup> proposes three possible mechanisms for the reaction;  $B_{ac}2$ ,  $B_{al}1$ , and  $B_{al}2$ . The B stands for base promoted, the ac and al for acyl oxygen cleavage or alkyl oxygen cleavage, respectively, and the 1 or 2 for first or second order kinetics. The mechanisms can be represented as follows:



The esters of pivalic acid were chosen for this study due to the steric hindrance imposed by the tertiary butyl group. This hindrance should inhibit reaction at the acyl carbon. Hence, this should limit the possible mechanisms to  $B_{al}1$  or  $B_{al}2$ . By simple kinetic studies these two mechanisms can be distinguished due to the difference in order of the reaction. Should the order found be second order and if there is still a question as to whether the mechanism is  $B_{ac}2$  or  $B_{al}2$  two possible methods are proposed to distinguish the two.

One method would be to label the hydroxide ion with  $^{18}O$ . From a Gas Chromatograph-Mass Spectra (GC-MS) of the products one could determine if this  $^{18}O$  label is now on the product alcohol or acid. In the case of  $B_{ac}2$  the  $^{18}O$  should appear in the acid and for  $B_{al}2$  in the alcohol. The other possible method is to use an optically active ester with the optical activity due to a chiral alkyl carbon on the carboxyl group. For the case of  $B_{ac}2$  the product alcohol should be in the same configuration and have the same rotation as the ester. If the mechanism was  $B_{al}2$  the product alcohol should show an inversion of rotation. For this study a GC-MS was not available and so the second method was employed using optically active sec-butyl pivaloate, the only optically active ester studied.

#### KINETIC STUDIES

The rate equations for simple first and second order saponifications are as follows:

- 1.) First Order:  $v_1 = k_1 [\text{ester}]$
- 2.) Second Order:  $v_2 = k_2 [\text{ester}][OH^-]$

For this study  $k_1$  will denote the rate constant for the first order reaction and  $k_2$  that for the second order reaction.

The problem then becomes one of designing an experiment to study the reaction. The first problem encountered is what to measure in the system. There is no good quantitative measure for the ester concentration or a product of the system which is convenient for use. However, it is easy to measure the hydroxide concentration of the system by a simple titration with a standardized acid, making sure the indicator changes in a region before one starts to titrate the pivaloate ion. In this case phenolphthalein was used as the indicator. From this point two methods were employed to study the system. Each will be discussed separately.

The first method, Type I, employs having equal ester and hydroxide ion concentration initially. As the reaction proceeds both concentrations will remain equal due to the stoichiometry of the reaction. Therefore the rate equations for first and second order reactions can be simplified to:

$$3.) v_1 = k_1 [\text{OH}^-]$$

$$4.) v_2 = k_2 [\text{OH}^-]^2$$

These equations can be manipulated further to give:

$$5.) \ln [\text{OH}^-] = -k_1 t + \ln [\text{OH}^-]_0$$

$$6.) 1/[\text{OH}^-] = k_2 t + 1/[\text{OH}^-]_0$$

For the first and second order reactions, respectively. Where  $t$  is time and  $[\text{OH}^-]_0$  is the initial concentration of hydroxide ions. It can be seen that the above are simply equations for a straight line. For the case of first order reaction (equation 5), a plot of  $\ln[\text{OH}^-]$  as a function of time should be

a straight line. A second order system should show a straight line if  $1/[\text{OH}^-]$  was plotted as a function of time. By using a linear regression on these two plots one can determine which is a better fit by the correlation coefficient of the plot. The one with the highest correlation will display the order of the reaction. The absolute value of the slope of the line, obtained by the linear regression, will be equal to the rate constant.

By monitoring the effect on the rate constants of varying the temperature it is possible to calculate the activation energy for the reaction. A plot of  $\ln k$  as a function of  $1/T$ , where  $T$  is temperature in Kelvin, gives an Arrhenius plot whose slope is equal to  $-E_a/R$ , where  $R$  is the gas constant and  $E_a$  is the activation energy of the reaction.

The second method, Type II, for determining the order of the reaction uses the solubility of the ester in water. For the Type I method an equimolar solvent mixture of ethanol and water was employed due to the limited solubility of the ester in water. If a two phase system, ester (organic) and aqueous, was employed at constant temperature the concentration of ester in the aqueous phase should be a constant equal to its saturation concentration. As the ester was consumed in the reaction it would be replaced by movement of ester from the organic phase into the aqueous phase. In this case the ester concentration could be considered a constant for the reaction. This would further simplify the rate equation for the first and second order reactions, respectively, to yield:

$$7.) \quad v_1 = k_1'$$

$$8.) \quad v_2 = k_2' [\text{OH}^-]$$

Where  $k_1'$  and  $k_2'$  denote  $k_1[\text{ester}]_{\text{eq}}$  and  $k_2[\text{ester}]_{\text{eq}}$  respectively, and where

$[\text{ester}]_{\text{eq}}$  is the saturation concentration of ester in the aqueous phase at a given temperature. These equations when integrated become:

$$9.) [\text{OH}^-] = k_1' + [\text{OH}^-]_0$$

$$10.) \ln [\text{OH}^-] = -k_2't + \ln [\text{OH}^-]_0$$

These equations are also equations representing a straight line with the absolute value of the slope being the rate constant. However in this case the rate constant will not be a true value since it also incorporates the solubility of the ester. Therefore these rate constants can not be used to determine the activation energy of the reaction, since the solubility of the ester will change with temperature.

#### EXPERIMENTAL PREPARATIONS

The following esters were prepared.

compound	boiling point ( $^{\circ}\text{C}$ )
methyl pivaloate	101
n-butyl pivaloate	162
isobutyl pivaloate	154
sec-butyl pivaloate	149
t-butyl pivaloate	134

#### Procedure:

- 1.) Dropwise addition of equimolar portions of pivaloyl chloride to the appropriate alcohol.
- 2.) Reflux for 2 to 3 hours.
- 3.) Wash 2 times with a NaOH solution, enough to twice over neutralize the product HCl.

4. Wash twice with distilled water.

5.) Distill the crude product over a glass bead column at the above indicated temperatures.

Optically active sec-butyl pivaloate was prepared by the above procedure using (-) sec-butanol. The product formed was (-) sec-butyl pivaloate.

#### Kinetic Studies

A HCl titrant was prepared to an approximate concentration of 0.1M. This solution was standardized with  $\text{Na}_2\text{CO}_3$  and its concentration was determined to be 0.0971M. This was the solution used for titration of reaction samples with phenolphthalein as an indicator. The size of the aliquot measured was 1.00ml.

##### Type I

A 50% by mole solution of ethanol and water was prepared for use as a solvent. The sample container employed was a Nalgene<sup>R</sup> wash bottle. The side arm spout was used to draw samples and a drying tube, containing ascarite, was put in a rubber stopper and replaced the screw top. This allowed for an open system with limited  $\text{CO}_2(\text{g})$  diffusion into the solution. Solutions were prepared with a hydroxide ion concentration of approximately 0.3M and an equal concentration of ester was added. The reaction container was then placed in a constant temperature bath and samples were drawn at different time intervals.

##### Type II (sec-butyl pivaloate only)

The same reaction container was employed as with Type I. The ester was added to distilled water so as to form a two phase system. This two phase system was immersed in a constant temperature bath for two days to allow the



ester concentration in the aqueous phase to equilibrate. After this period NaOH pellets were added to the system to achieve a concentration between 0.3M and 1.0M. The system was then placed again in the constant temperature bath and samples were drawn at different time intervals.

#### Optical Rotation Study (sec-butyl pivaloate only)

A solution was prepared in a manner identical to the Type I kinetic study except the optically active ester was used. The rotation of the sample was taken as a function of time over a period of approximately 3 half lives of the reaction. At this point it became impossible to further measure the rotation of the solution. The solution had changed from clear to a very dark brown almost opaque solution. The polarimeter was reading a limit of light so no further rotations were taken. At the end of only 3 half lives the reaction had not proceeded enough for the study of a sign change to be complete. At this point the rotation was still approaching zero. If the sign of the product was inverted it could still be masked by the rotation of the ester. A second study was undertaken at this point. The same conditions were employed except that the solution was allowed to run in excess of 30 half lives before any rotations were taken. It was believed that consistently removing the sample from the reaction container to measure a rotation might have been contaminating the sample. Hence at the end of more than 30 half lives the rotation of the sample was measured. Unfortunately, the solution had again darkened and was at the limit of light for the polarimeter. The reaction solution was then distilled by a simple vacuum distillation. The distillate gathered was approximately half the total initial sample volume. A Gas Chromatograph of this sample was run and contained a significant peak at a time equimobil to sec-butanol. Also, there was no peak at a time equimobil to sec-butyl

pivaloate. A rotation was run on this distillate and the rotation measured is assumed to be due to the rotation of the product sec-butanol.

## RESULTS

A GC was run on all studies to check for the presence of products of a possible elimination reaction. No elimination products, mainly butenes, were found so the possibility of an elimination reaction occurring was dismissed.

### Type I kinetic runs

The following is a summary of the results of the Type I kinetic runs. The rate constants were calculated by taking the absolute value of the slope from a linear regression of the raw data using equations 5 and 6.

Ester	T(°C)	$k_1$	correlation	$k_2$	correlation
		(1/min)		(1/min M)	
t-butyl	50	$1.82 \times 10^{-6}$	.832	$6.66 \times 10^{-6}$	.829
	37	$1.16 \times 10^{-7}$	.066	$3.95 \times 10^{-7}$	.064
	25	$4.76 \times 10^{-7}$	.246	$1.68 \times 10^{-6}$	.242
sec-butyl	50	$6.51 \times 10^{-5}$	.979	$9.17 \times 10^{-4}$	.980
	37	$2.69 \times 10^{-5}$	.981	$2.50 \times 10^{-4}$	.994
	25	$1.14 \times 10^{-5}$	.989	$6.97 \times 10^{-5}$	.993
isobutyl	50	$5.07 \times 10^{-4}$	.964	$1.54 \times 10^{-2}$	.990
	37	$2.57 \times 10^{-4}$	.996	$8.47 \times 10^{-3}$	.949
	25	$1.16 \times 10^{-4}$	.998	$1.26 \times 10^{-3}$	.990

Ester	T(°C)	$k_1$	correlation	$k_2$	correlation
		(1/min)		(1/min M)	
n-butyl	50	$1.24 \times 10^{-3}$	.991	$2.32 \times 10^{-2}$	.983
	37	$5.43 \times 10^{-4}$	.990	$1.81 \times 10^{-2}$	.957
	25	$2.00 \times 10^{-4}$	.975	$3.31 \times 10^{-3}$	.927
methyl	50	$1.26 \times 10^{-2}$	.908	$2.69 \times 10^{-1}$	.998
	37	$6.96 \times 10^{-3}$	.963	$1.33 \times 10^{-1}$	.998
	25	$2.00 \times 10^{-3}$	.959	$5.54 \times 10^{-2}$	.992

From these rate constants the activation energies were calculated assuming both first and second order kinetics. The values below were calculated using linear regression on a Arrhenius plot. The correlation coefficients reported are obtained from this plot.  $E_1$  and  $E_2$  represent the activation energies for first and second order respectively.

Ester	$E_1$ (kJ/mole)	Correlation	$E_2$ (kJ/mole)	Correlation
t-butyl	42.9	.487	44.0	.487
sec-butyl	55.6	.999	82.4	1.000
isobutyl	47.1	.999	80.0	.957
n-butyl	58.2	.998	62.3	.918
methyl	58.9	.980	50.5	.998

#### Type II kinetic runs

The following is a summary of the results of the Type II kinetic study of sec-butyl pivaloate. The rate constants were calculated by taking the absolute value of the slope from a linear regression of the raw data using equations 9 and 10.

T(°C)	$k_1'$ (M/day)	correlation	$k_2'$ (l/day)	correlation
25	$5.09 \times 10^{-4}$	.995	$1.36 \times 10^{-3}$	.995
25	$7.37 \times 10^{-4}$	.841	$1.32 \times 10^{-3}$	.862
25	$5.23 \times 10^{-4}$	.998	$6.85 \times 10^{-4}$	.998
37	$1.22 \times 10^{-3}$	.939	$3.33 \times 10^{-3}$	.963
37	$1.88 \times 10^{-3}$	.699	$3.14 \times 10^{-3}$	.774
37	$2.63 \times 10^{-3}$	.596	$2.87 \times 10^{-3}$	.670
50	$2.09 \times 10^{-3}$	.948	$4.92 \times 10^{-3}$	.950
50	$1.01 \times 10^{-2}$	.495	$1.46 \times 10^{-2}$	.534
50	$1.09 \times 10^{-2}$	.514	$1.24 \times 10^{-2}$	.552

Average values weighted by correlation coefficient.

T(°C)	$k_1'$	$k_2'$
25	$5.81 \times 10^{-4}$	$1.11 \times 10^{-3}$
37	$1.80 \times 10^{-3}$	$3.14 \times 10^{-3}$
50	$6.42 \times 10^{-3}$	$9.49 \times 10^{-3}$

Optical rotation study of sec-butyl pivaloate (Type I):

Initial rotation of crude ester = -16.01

First Run:

Kinetic run: T = 50°C Moles NaOH =  $6.6 \times 10^{-3}$  25ml solution  
Moles sec-butyl pivaloate =  $6.6 \times 10^{-3}$

t(hrs)	rotation	t(hrs)	rotation
0	-0.69	69	-0.32
1	-0.66	91	-0.31
2	-0.68	113	-0.26
7	-0.60	137	-0.22
11	-0.56	185	-0.19
21	-0.53	209	limit
32	-0.46		
46	-0.43		

Second run:

Same preparation, solution allowed to stand 4 months.

Final rotation of solution - limit

Final rotation of distillate of reaction solution = -0.12

The distillate is approximately one half of the entire solution volume.

#### DISCUSSION

Before delving into a discussion of mechanisms for the reactions studied it is first necessary to further discuss the methods employed in the studies. The results of the majority of the kinetic studies are not as discriminating as expected. With differences in correlation coefficients of at times less than 0.01 it is difficult to say the reaction is clearly first or second order.

There are a few problems associated with both methods. One of the most important would be the diffusion of  $\text{CO}_2(\text{g})$  into the reaction container and formation of carbonates. This would tend to reduce the hydroxide concentra-

tion. For the Type I reactions  $\text{CO}_2(\text{g})$  was removed by the ascarite tube which was periodically replaced. No carbonate precipitate was observed in the solution and it was concluded that  $\text{CO}_2(\text{g})$  contamination was not a significant problem. For the Type II method a long glass tube bent over at the top was used. The organic layer above the aqueous layer should slow down the diffusion of  $\text{CO}_2(\text{g})$  into the aqueous phase and again no precipitate was observed. The tube was used primarily to reflux the reaction solution so evaporation would not concentrate the hydroxide.

Another possible problem could be the formation of the dark brown compound which impeded the optical rotation study. The cause of the color development is unknown. A GC trace of the solution showed no unaccountable peaks. In the Type II method the brown was only noticed in the organic layer. One could postulate that this darkening is due to some association of the reactants and/or products over time that showed a temperature dependence, since the solutions at higher temperature turned a darker color.

A reaction occurring with the container could cause a problem. However, most of the compounds used, other than hydroxide ion, are not very reactive. The hydroxide does not appear to be reacting since in the case of the study of t-butyl pivaloate the hydroxide concentration hardly changed. If substances such as the ester were absorbed into the reaction vessel and held there this could affect the reaction but this seems unlikely. The reaction container cleaned out easily with the ethanol and water solvent. Also with the Type II method this would not matter as long as the ester concentration was constant.

In the Type I studies the solvent contains a mixture of ethanol and water. With ethanol present in the solution it is possible that a transester-

ification is occurring. Gas chromatographic analysis of both the sec-butyl and t-butyl ester studies showed small amounts of the ethyl ester present in the solution after an extended period of time. Whether this small amount had a great effect on the study cannot be answered for certain. Since the t-butyl and sec-butyl esters have very slow rates of saponification one would predict an even slower rate of transesterification. Likewise since the methyl ester reacts fairly rapidly one would predict the ethyl ester would also react fairly rapidly. Once the transesterification occurs its effect on the kinetic study should be one of speeding up the depletion of hydroxide. However, in the case of t-butyl pivaloate, there was hardly any consumption of hydroxide yet what appeared to be an ethyl pivaloate peak on the GC of about the same size as in the sec-butyl ester reaction solution. Hence it was concluded that transesterification did not significantly affect the reaction.

The Type II study is a unique method. The major limiting factor in this study is whether or not the ester concentration is constant over the course of the run. A GC analysis of the solution as the reaction proceeds indicates that the ester concentration remains constant to one significant figure. Only one significant figure can be reported due to the ester's low concentration and the increasing concentration of the products which resulted in increasingly difficult separation of the peaks. Whether the concentration is truly constant to more significant figures is as yet uncertain.

Another aspect of this method worthy of investigation is whether or not the reaction being monitored is occurring at the interface of the organic and aqueous phases. To test this, samples were pipetted from different depths of the reaction container. These samples were titrated and showed the same hydroxide concentration, within the error of the titration. Hence there is no

gradient of hydroxide ions in the aqueous phase towards the interface. Also, the reaction of the sec-butyl pivaloate is extremely slow in concentrated solution so in this case the reaction must be even slower since the solubility of the ester in the aqueous phase is extremely low. Therefore the diffusion of ester into the solution should be faster than the reaction itself so it is unlikely that the reaction is taking place at the interface.

Whether or not these possible problems are affecting the measurements of the system is a key question. For the Type I method the answer is probably no. Most problems encountered in this method would tend to decrease the hydroxide concentration. Again, certain extended runs with the t-butyl ester showed no significant change in hydroxide concentration. For the Type II method the answer is not as clear. The major problem here would be if the ester concentration was not constant in the aqueous phase and by how much of a factor it changed over the course of the run. This is not answered. However since the majority of the correlations and data agree with the Type I method for the same ester one would say the method is fairly sound.

A problem could arise in the procedure if the brown coloration observed is in any way changing the reaction. If the discoloration is due to a different association of the species in solution this association might cause a change in the mechanism. One mechanism might be more favorable when the solution is uncolored but another might be favored when the solution is discolored. Since the reaction does not proceed in the reverse direction very readily it is unlikely that any association of the products would affect the kinetics of the reaction. If there was an association of the reactants that might change the most favored position of attack then the kinetics could very well change. Neither of these possibilities has been studied.



Why then is there no significant difference in the correlation coefficients for first order versus second order plots? The most likely explanation is that in most cases mechanisms are competing against each other. In most cases then at least two mechanisms would be occurring. In all cases, except in the case of the isobutyl ester, the correlation coefficients for one order were always greater than the correlation coefficients for the other order. From this one should tend to think that one order is more prevalent than the other but both are occurring.

Since it is apparent that both mechanisms are occurring it would be useful to calculate the overall order of the reaction. Unless something unusual is occurring the order of the reaction with respect to the ester should be first order. Hence it should suffice to calculate the order with respect to hydroxide. To do this one must start with the following rate equation:

$$11.) \quad v = k [\text{ester}] [\text{OH-}]^x$$

In this case we will look only at the Type I kinetic studies since this method was used on all esters. For this method the equation will become:

$$12.) \quad v = k [\text{OH-}]^{x+1}$$

This equation then integrates to yield:

$$13.) \quad 1/x[\text{OH-}]^x = kt + 1/x[\text{OH-}]_0^x$$

If a combination of first and second order are occurring then  $x$  should exist in the open interval  $(0,1)$ . A non-linear regression could be performed on this equation to solve for  $x$ . For this case a non-linear regression program was not available. Another approach would be to vary  $x$  between zero and one.

For each case of  $x$  one could plot  $1/x[\text{OH}^-]^x$  as a function of time and by a linear regression calculate the correlation coefficient. If the correlation coefficient was plotted as a function of  $x$ , the order with respect to hydroxide, one could find the point where the correlation reaches a maximum. At this point the value of  $x$  would be the order of the reaction with respect to hydroxide. If this plot is highest at one of its ends, where the order is first or zero order with respect to hydroxide, then one can say the reaction is one mechanism or the other, depending upon which correlation coefficient is the highest, and not a combination of both mechanisms. This method was applied to these data and the resulting graphs can be found in Appendix C. This technique allows one to determine, fairly precisely, the order of the reaction with respect to hydroxide concentration. However, it does not allow one to say that a certain percentage of the overall reaction is one mechanism and the rest due to a second mechanism.

Presently a method will be proposed to calculate the percentage of the overall reaction due to first order and second order reactions. In addition this method would allow one to also calculate the specific rate constants and activation energies for the reactions. This method requires the use of a non-linear regression which was not available for this study. Hence the following calculations are only proposed and as of the present time not available.

Again, looking at the Type I studies, if one were to solve equations 5 and 6, respectively, for the hydroxide concentration one would have:

$$14.) [\text{OH}^-] = e^{(-k_1 t + \ln[\text{OH}^-]_0)}$$

$$15.) [\text{OH}^-] = 1/(k_2 t + 1/[\text{OH}^-]_0)$$

Since in most cases both first and second order reaction are occurring one

could say a certain factor of hydroxide concentration,  $y$ , was due to first order reaction and another fraction,  $z$ , was due to second order reaction where:

$$16.) \quad y + z = 1$$

This would give that the hydroxide concentration due to first order and second order, respectively, for the overall reaction would be:

$$17.) \quad y[\text{OH}^-] = e^{(-k_1 t + \ln[\text{OH}^-]_0)}$$

$$18.) \quad z[\text{OH}^-] = 1/(k_2 t + 1/[\text{OH}^-]_0)$$

If equations 17 and 18 were added the sum would yield:

$$19.) \quad [\text{OH}^-] = e^{(-k_1 t + \ln[\text{OH}^-]_0)} + 1/(k_2 t + 1/[\text{OH}^-]_0)$$

From this equation with a non-linear regression one could solve for the specific rate constants,  $k_1$  and  $k_2$ , of the first and second order reaction. These rate constants should be much closer to true values than those calculated previously since this equation does not take for granted that one mechanism only is occurring. If equation 19 is multiplied by negative one and differentiated with respect to time the resulting equation would be:

$$20.) \quad v = k_1 e^{(-k_1 t + \ln[\text{OH}^-]_0)} + k_2 (1/(k_2 + 1/[\text{OH}^-]_0)^2)$$

But what is in brackets is just  $y[\text{OH}^-]$  and  $z^2[\text{OH}^-]$  so this equation becomes:

$$21.) \quad v = k_1 y[\text{OH}^-] + k_2 z^2[\text{OH}^-]^2$$

For convenience let:

$$22.) \quad k_1 y = k_y$$

$$23.) \quad k_2 z^2 = k_z$$

This makes equation 21:

$$24.) \quad v = k_y [\text{OH}\cdot] + k_z [\text{OH}\cdot]^2$$

Integrating this equation as has been previously done for rate equations one arrives at:

$$25.) \quad \log((k_y + k_z [\text{OH}\cdot]) / [\text{OH}\cdot]) = k_y t + \log((k_y + k_z [\text{OH}\cdot]_0) / [\text{OH}\cdot]_0)$$

A non-linear regression on this equation could then solve for  $k_y$  and  $k_z$ . With these values and the values for  $k_1$  and  $k_2$  one could solve for  $y$  and  $z$  using equations 22 and 23.

The values calculated for  $k_1$  and  $k_2$  by the above method should allow one to calculate the activation energy of the first order mechanism and second order mechanism by again using an Arrhenius plot. Previously calculated values for the activation energy are not independent values. Each was calculated assuming the overall reaction was one mechanism or the other. The values calculated from these new rate constants should be more precise. However, the previously calculated activation energies should be good approximations since the correlation coefficients for these plots approached one.

Before discussing the mechanistic possibilities for the reactions studied it becomes important to remember the reliability of any calculated values. The order of the overall reaction is fairly well illustrated by the plots in Appendix C. The values calculated for  $k_1$  and  $k_2$  can be taken as fairly good qualitative measures of the rate, however as quantitative measures they are not very reliable. These calculated values for the Type I method only

represent one experimental run. The reproducibility of these numbers is unknown. Also these numbers were calculated under the assumption only one mechanism is occurring. This again would lead to the fact that the activation energies calculated are qualitative values and not quantitative ones since they were calculated from the aforementioned rate constants.

The consistency in the data for the study of t-butyl pivaloate is poor. The correlation coefficients for the plots lack a straight line fit except for the study performed at 50°C. From Figure 1 in Appendix C we see that for the study performed at 50°C the order with respect to hydroxide appears to be zero. Hence the mechanism for the reaction would be  $B_{al}1$ . This would be the expected result due to the extreme steric hindrance to a bimolecular reaction imposed by the t-butyl groups on either side of the carboxyl group. The calculated activation energy is questionable due to the low correlation for the Arrhenius plot and unreliability of the calculated rate constants used in this plot.

The most completely studied compound was sec-butyl pivaloate. This was the only compound studied by the Type II method and an optical rotation study. The Type II kinetic studies showed fairly consistently that the second order reaction was more prominent. From the Type I study we also see this. Figure 2 in Appendix C shows the order with respect to the hydroxide concentration at several temperatures. There does not appear to be any pattern with respect to the order as a function of temperature. The optical rotation study shows that the product alcohol has the same sign as the reactant ester and thus shows that the reaction proceeds with retention of configuration. This shows that the second order reaction is not  $B_{al}2$  as expected but rather  $B_{ac}2$ . The activation energy calculated for this second order reaction is very high,

showing the difficulty for the acyl attack. The first order mechanism occurring must be  $B_{al}^1$ . Hence the total combined reaction is one of  $B_{al}^1$  and  $B_{ac}^2$  competing.

The Type I kinetic study of isobutyl pivaloate shows the order with respect to hydroxide concentration to shift with temperature. As the temperature increases, the order with respect to hydroxide shifts from zero to one (See Figure 3 Appendix C). Hence the overall reaction starts out as mostly first order and as the temperature increases the second order reaction becomes more prominent. The first order reaction is clearly  $B_{al}^1$ , however whether the second order reaction is  $B_{al}^2$  or  $B_{ac}^2$  is questionable. Due to the high activation energy calculated, nearly equal to that of the second order reaction for sec-butyl pivaloate, one would expect the mechanism to be  $B_{ac}^2$ . To verify this is a mass spectral study with  $^{18}O$  would be necessary.

For n-butyl pivaloate basically the same trend is shown as with isobutyl pivaloate but, in this case, even at higher temperature, the first order reaction is still dominant (See Figure 4 Appendix C). Again, the first order mechanism is  $B_{al}^1$ . Due to the lower calculated activation energy for the second order reaction one would expect that in this case the mechanism is  $B_{al}^2$  but again this can only be supported by a mass spectral analysis with  $^{18}O$ .

In the case of methyl pivaloate one would expect the attack on the molecule to occur at the alkyl carbon specifically due to the minimal steric hindrance imposed by the methyl group. In the cases of the butyl esters the butyl groups imposed enough steric hindrance to attack that one could not be sure whether attack was occurring at the alkyl or acyl carbon for the second order mechanism. In this study it was shown that methyl pivaloate reacted primarily

by a second order mechanism. As the temperature of the system was increased one can see from figure 5 in Appendix C that the order with respect to hydroxide concentration increased to one at 50°C. From this temperature on one would expect the reaction to show second order kinetics. The activation energy calculated for the second order mechanism is the lowest for those calculated values, excluding that calculated for t-butyl pivaloate due to the extremely low correlation coefficient for the Arrhenius plot. Also, in this case one can see that for the first time the activation energy for the second order mechanism is less than that for the first order mechanism. Hence in this case the second order mechanism should be  $B_{al}2$  due to the much favored alkyl over acyl attack. To verify this one would again have to perform a mass spectral study with  $^{18}O$ .

#### SUMMARY

Kinetic studies of the saponification of several esters of pivalic acid have been performed. From the data accumulated from these studies rate constants and activation energies have been calculated and mechanistic possibilities for the reactions have been proposed. In addition a method has been proposed to specifically determine the percentage of the overall reaction which is first order and that which is second order. This method will also allow one to calculate specifically the rate constants and activation energies for the first and second order reactions with no imposed assumptions.

#### REFERENCE

- [1] Ingold, C.K., Structure and Mechanism in Organic Chemistry,  
Second Edition, Cornell University Press, Ithaca, New York, 1969, pp.  
1129-1144.

RAW DATA - Type I kinetic runs

t-butyl pivaloate:

T=50°C      moles NaOH= 0.126

moles ester= 0.126

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln [OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln [OH <sup>-</sup> ]
0	.297	3.36	-1.214	18237	.276	3.62	-1.287
123	.291	3.43	-1.234	23147	.277	3.61	-1.284
310	.292	3.42	-1.231	24450	.278	3.59	-1.280
1057	.294	3.40	-1.224	27476	.274	3.65	-1.295
2892	.293	3.41	-1.228	30262	.272	3.67	-1.302
4218	.294	3.40	-1.224	34588	.271	3.69	-1.306
5505	.287	3.48	-1.248	37538	.273	3.66	-1.298
7222	.283	3.53	-1.262	45983	.262	3.81	-1.339
8689	.283	3.53	-1.262	48880	.265	3.81	-1.328
13113	.274	3.65	-1.295	51554	.267	3.74	-1.321
14707	.274	3.65	-1.295	54762	.261	3.83	-1.343
15852	.249	4.01	-1.390	69180	.253	3.95	-1.374
17293	.277	3.61	-1.284	83665	.251	3.98	-1.382



T= 37°C

moles NaOH= 0.126

moles ester= 0.126

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.292	3.42	-1.231	14686	.282	3.55	-1.266
104	.295	3.39	-1.221	15892	.276	3.62	-1.287
294	.295	3.39	-1.221	17276	.292	3.42	-1.231
1043	.296	3.38	-1.217	18221	.291	3.44	-1.234
2878	.294	3.40	-1.224	23132	.295	3.39	-1.221
4202	.291	3.44	-1.234	24437	.294	3.40	-1.224
5489	.293	3.41	-1.228	27461	.295	3.39	-1.221
7206	.287	3.48	-1.248	30246	.294	3.40	-1.224
8668	.280	3.57	-1.273	34584	.283	3.53	-1.262
13101	.282	3.55	-1.266	37471	.294	3.40	-1.224

T= 25°C

moles NaOH= 0.121

moles ester= 0.121

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.276	3.62	-1.287	13094	.267	3.75	-1.321
290	.285	3.51	-1.255	14682	.283	3.53	-1.262
1042	.278	3.60	-1.280	15886	.273	3.66	-1.298
2874	.281	3.56	-1.269	17274	.282	3.55	-1.266
4201	.282	3.55	-1.266	23128	.281	3.56	-1.269
5483	.275	3.64	-1.291	27457	.281	3.56	-1.269
7197	.277	3.61	-1.284	30238	.281	3.56	-1.269
8664	.265	3.77	-1.328	34589	.285	3.51	-1.255

Sec-butyl pivaloate

T= 50°C

moles NaOH= 0.127

moles ester= 0.127

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.296	3.38	-1.217	14716	.0728	13.74	-2.620
128	.285	3.51	-1.255	15920	.0631	15.85	-2.763
316	.272	3.68	-1.302	17300	.0621	16.10	-1.779
1063	.237	4.22	-1.440	18245	.0592	16.89	-2.827
2897	.184	5.43	-1.693	23151	.0447	22.37	-3.108
4224	.155	6.45	-1.864	24456	.0427	23.42	-3.154
5511	.141	7.09	-1.959	27482	.0408	24.51	-3.199
7231	.121	8.26	-2.112	30271	.0379	26.39	-3.273
8534	.115	8.70	-2.163	34597	.0262	38.17	-3.642
13131	.0922	10.85	-2.384	37550	.0243	41.15	-3.717

T= 37°C

moles NaOH= 0.126

moles ester= 0.126

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.291	3.44	-1.234	27462	.105	9.52	-2.254
110	.286	3.50	-1.252	30248	.101	9.90	-2.293
296	.292	3.42	-1.231	34573	.0874	11.44	-2.437
1045	.271	3.69	-1.306	35891	.0777	12.87	-2.555
2879	.248	4.03	-1.394	37524	.0806	12.41	-2.518
4202	.232	4.31	-1.461	41789	.0748	13.37	-2.593
5490	.219	4.57	-1.519	44718	.0738	13.55	-2.606
7209	.201	4.98	-1.604	46009	.0719	13.91	-2.632

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
8672	.180	5.56	-1.715	48882	.0680	14.71	-2.688
13104	.167	5.99	-1.790	51554	.0660	15.15	-2.718
14691	.147	6.80	-1.917	54677	.0582	17.18	-2.844
15897	.133	7.52	-2.017	57631	.0544	18.38	-2.911
17279	.141	7.09	-1.959	63559	.0486	20.58	-3.024
18225	.135	7.41	-2.002	69167	.0486	20.58	-3.024
23134	.116	8.62	-2.154				

T= 25°C

moles NaOH= 0.114

moles ester= 0.114

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.263	3.80	-1.336	27454	.170	5.88	-1.772
290	.258	3.88	-1.355	30237	.169	5.92	-1.778
1044	.259	3.86	-1.351	34570	.175	6.67	-1.852
2875	.245	4.08	-1.406	37507	.173	5.78	-1.754
4206	.238	4.20	-1.435	41765	.151	6.62	-1.890
5483	.233	4.29	-1.457	46001	.140	7.14	-1.966
7158	.223	4.48	-1.501	48883	.137	7.30	-1.988
11545	.216	4.63	-1.532	51542	.140	7.14	-1.966
13092	.207	4.83	-1.575	54633	.130	7.69	-2.040
14682	.199	5.03	-1.614	57746	.123	8.13	-2.096
15882	.193	5.18	-1.645	63535	.121	8.26	-2.112
17274	.201	4.98	-1.604	69140	.114	8.77	-2.172
18209	.198	5.05	-1.619	83617	.102	9.80	-2.283
23128	.184	5.43	-1.693				

Isobutyl pivaloate

T= 50°C

moles NaOH=  $3.08 \times 10^{-2}$

moles ester=  $3.08 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.193	5.18	-1.645	1505	.0544	18.4	-2.911
206	.156	6.41	-1.858	1831	.0427	23.4	-3.154
355	.132	7.58	-2.025	3051	.0223	44.8	-3.803
425	.126	7.94	-2.071	5778	.0107	93.5	-4.538
1309	.0592	16.9	-2.827				

T= 37°C

moles NaOH=  $3.08 \times 10^{-2}$

moles ester=  $3.08 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.194	5.15	-1.640	1838	.100	10.0	-2.303
245	.175	5.71	-1.743	3121	.0680	14.7	-2.688
383	.170	5.88	-1.772	5796	.0378	26.5	-3.275
1318	.121	8.26	-2.112	11926	.00874	114.	-4.740

T= 25°C

moles NaOH =  $3.05 \times 10^{-2}$

moles ester =  $3.05 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.193	5.18	-1.645	3148	.124	8.06	-2.087
267	.179	5.59	-1.720	5808	.0893	11.2	-2.416
390	.182	5.49	-1.704	8891	.0670	14.9	-2.703
1325	.158	6.33	-1.845	11939	.0476	21.0	-3.045
1843	.151	6.62	-1.890				

N-butyl pivaloate

T= 50°C

moles NaOH =  $3.10 \times 10^{-2}$

moles ester =  $3.10 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.204	4.90	-1.590	1329	.0291	34.4	-3.537
223	.129	7.75	-2.048	1525	.0282	35.5	-3.568
339	.104	9.62	-2.263	1851	.0184	54.3	-3.995
444	.0864	11.6	-2.449				

T= 37°C

moles NaOH =  $3.23 \times 10^{-2}$

moles ester =  $3.23 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.215	4.65	-1.537	1860	.0524	19.1	-2.949
266	.166	6.02	-1.796	3144	.0291	34.4	-3.537
405	.149	6.71	-1.904	5820	.00874	114.	-4.740
1339	.0738	13.6	-2.606				

T= 25°C

moles NaOH =  $2.95 \times 10^{-2}$

moles ester =  $2.95 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.191	5.24	-1.655	1863	.115	8.70	-2.163
287	.174	5.75	-1.748	3165	.0767	13.0	-2.568
409	.166	6.02	-1.796	8830	.0408	24.5	-3.199
1344	.134	7.46	-2.010	8927	.0233	42.9	-3.759

Methyl pivaloate

T= 50°C

moles NaOH =  $3.23 \times 10^{-2}$

moles ester =  $3.23 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.243	4.12	-1.415	83	.0359	27.9	-3.327
49	.0583	17.2	-2.842	119	.0262	38.2	-3.642
66	.0456	21.9	-3.088	189	.0184	54.3	-3.995

T= 37°C

moles NaOH =  $2.95 \times 10^{-2}$

moles ester =  $2.95 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.215	4.65	-1.537	186	.0350	28.6	-3.352
39	.115	8.70	-2.163	320	.0214	46.7	-3.844
110	.0592	16.9	-2.827				

T= 25°C

moles NaOH =  $3.30 \times 10^{-2}$

moles ester =  $3.30 \times 10^{-2}$

t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(min)	[OH <sup>-</sup> ]	1/[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.244	4.10	-1.411	309	.0631	15.8	-2.763
36	.175	5.71	-1.743	507	.0427	23.4	-3.154
99	.121	8.26	-2.112	1357	.0126	79.4	-4.374
175	.0922	10.8	-2.384				

RAW DATA - Type II kinetic runs

Sec-butyl pivaloate

T = 25°C

Run 1

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.414	-0.882	11	.403	-0.909
1	.406	-0.901	15	.403	-0.909
2	.408	-0.896	25	.401	-0.914
3	.413	-0.884	40	.391	-0.939
4	.408	-0.896	63	.379	-0.970
5	.408	-0.896	106	.358	-1.027
7	.408	-0.896	149	.334	-1.097

Run 2

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.641	-0.445	11	.573	-0.557
1	.634	-0.456	15	.565	-0.571
2	.610	-0.494	25	.553	-0.592
3	.602	-0.507	40	.553	-0.592
4	.590	-0.528	63	.539	-0.618
5	.578	-0.548	106	.522	-0.650
7	.578	-0.548	149	.502	-0.689

## Run 3

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.801	-0.222	52	.772	-0.259
4	.799	-0.224	95	.751	-0.286
14	.796	-0.228	138	.731	-0.313
29	.789	-0.237	154	.721	-0.327

T = 37°C

## Run 1

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	.498	-0.697	14	.416	-0.877
1	.476	-0.742	24	.408	-0.896
2	.454	-0.790	39	.393	-0.934
3	.425	-0.856	62	.359	-1.024
4	.425	-0.856	112	.313	-1.162
6	.420	-0.868	150	.273	-1.298
10	.422	-0.863			

## Run 2

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
1	.921	-0.0823	11	.599	-0.512
2	.819	-0.199	15	.600	-0.511
3	.741	-0.300	25	.590	-0.528
4	.685	-0.378	33	.595	-0.519
4	.660	-0.416	40	.571	-0.560
5	.651	-0.429	63	.542	-0.612



7	.607	-0.499	113	.486	-0.722
8	.595	-0.519	151	.454	-0.790

Run 3

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
1	1.47	0.385	15	.840	-0.174
2	1.18	0.166	25	.828	-0.189
3	1.07	0.0677	40	.835	-0.180
4	.979	-0.0212	63	.770	-0.261
5	.922	-0.0812	113	.751	-0.286
7	.845	-0.168	151	.688	-0.374
8	.853	-0.159			

T = 50°C

Run 1

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
1	.450	-0.799	5	.447	-0.805
2	.437	-0.828	7	.430	-0.844
3	.450	-0.799	15	.422	-0.863
4	.447	-0.805	25	.398	-0.921

Run 2

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	1.03	0.0296	5	.558	-0.583
1	.743	-0.297	7	.558	-0.583
2	.561	-0.578	15	.527	-0.641

3	.561	-0.578	25	.522	-0.650
4	.571	-0.560			

Run 3

t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]	t(days)	[OH <sup>-</sup> ]	ln[OH <sup>-</sup> ]
0	1.24	0.215	5	.733	-0.311
1	.911	-0.0932	7	.733	-0.311
2	.809	-0.212	15	.717	-0.333
3	.755	-0.281	25	.699	-0.358
4	.733	-0.311			

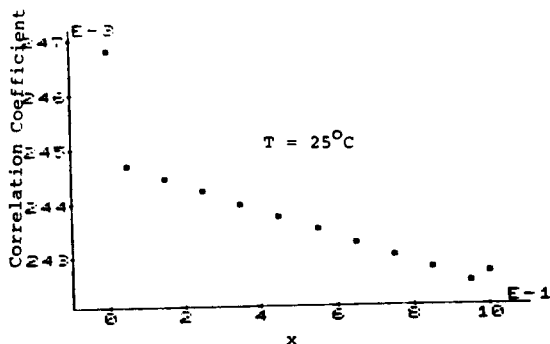
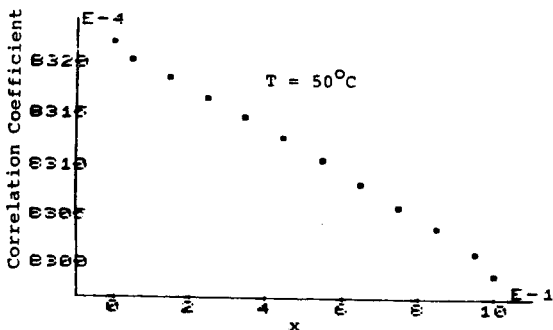
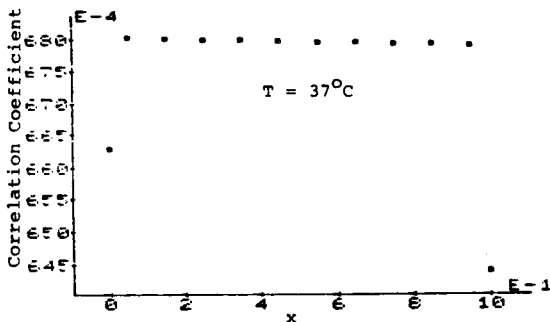


Figure 1

Graph of correlation coefficient of a plot of  $1/x[\text{OH}^-]^x$  vs time as a function of  $x$ , the order with respect to hydroxide ion.

t-butyl pivaloate



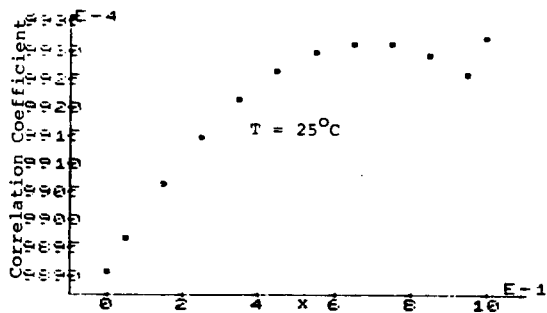


Figure 2

Graph of correlation coefficient of a plot of  $1/x[\text{OH}^-]^x$  vs time as a function of  $x$ , the order with respect to hydroxide ion.

sec-butyl pivaloate

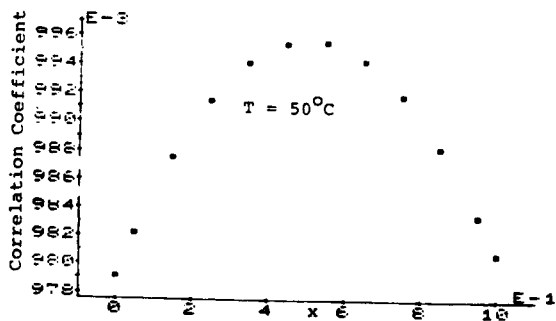
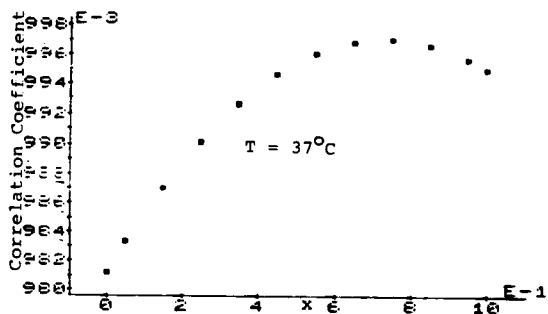
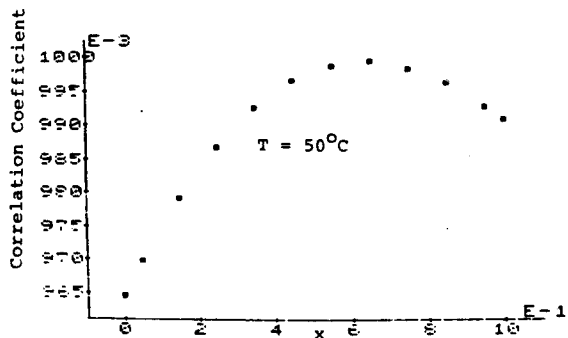
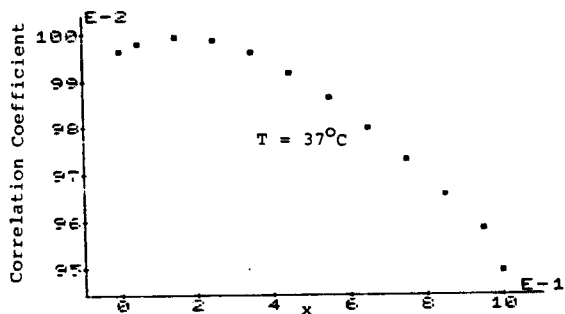
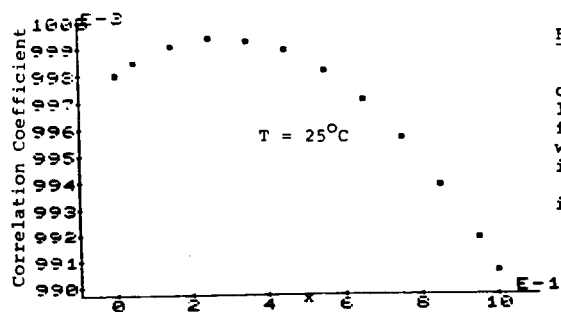


Figure 3

Graph of correlation coefficient of a plot of  $1/x[\text{OH}^-]^x$  vs time as a function of  $x$ , the order with respect to hydroxide ion.

isobutyl pivaloate



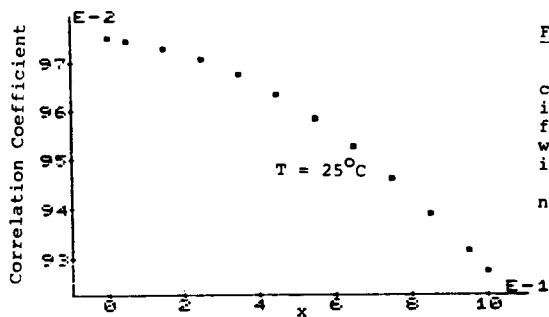


Figure 4

Graph of correlation coefficient of a plot of  $i/x[\text{OH}^-]^x$  vs time as a function of  $x$ , the order with respect to hydroxide ion.

n-butyl pivaloate

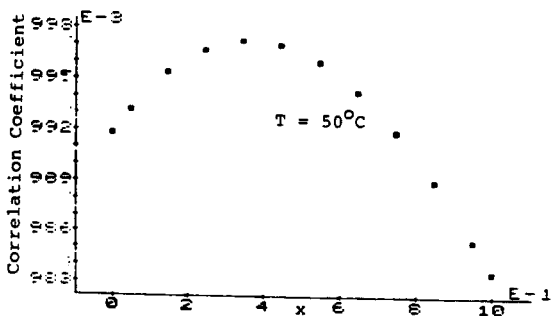
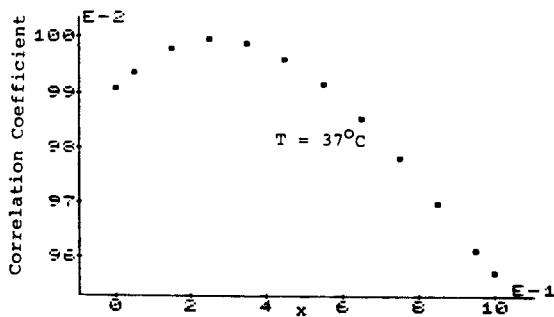


Figure 5

Graph of correlation coefficient of a plot of  $1/x[\text{OH}^-]^x$  vs time as a function of  $x$ , the order with respect to hydroxide ion.

methyl pivaloate

