

Pressure Dependence of Hydrolysis – Aminolysis of Long Chain Esters. Activation Volumes of Hydrophobic Interactions

EDDIE MORILD* and GRO AKSNES

Department of Chemistry, Realfagbygget, University of Bergen, N-5014 Bergen-U., Norway

The hydrolysis/aminolysis reaction of long chain *p*-nitrophenyl esters by long chain amines has been used as a model reaction for time-dependent hydrophobic interactions. The kinetics of the reactions of various combinations of esters and amines have been investigated in the pressure interval 0.1 – 150 MPa. The dependence of the three kinetic constants on pressure has been determined and activation volumes associated with each have been calculated. From relations between activation volumes and chain lengths, group contributions to the activation volumes could be estimated. A new catalytic mechanism is sketched for amine catalyzed hydrolysis. The reaction rates increased with pressure for all reactions. The results showed that there was an activation volume of about $+1 \text{ cm}^3 \text{ mol}^{-1}$ per pair of CH_2 -groups in contact.

We have for some time been concerned with the volume changes that take place in enzymatic reactions, because these volume changes determine the change of reaction rates with pressure. A knowledge of the pressure dependence of enzymatic reaction rates is in turn important for a proper understanding of deep sea biology.

A fairly large amount of information exists about volume changes in bond formation and breakage,¹ and also about volume changes in electrostatic interactions and hydrogen bonds.^{2,3} However, not much is known about the volume changes in hydrophobic interactions.⁴ From X-ray structure studies of enzymes it has been found that active sites may have parts dominated by hydrophobic groups. It is believed that the hydrophobic part of the substrates interact favourably with the hydrophobic

part of the active sites, and that this partly is a basis for a rapid turn-over in enzyme kinetics. That hydrophobic interactions really may be responsible for increased reaction rates has been demonstrated by Blyth and Knowles^{5,6} and by Oakenfull.^{7–9}

Some work has been done on volume changes of hydrophobic interactions in equilibrium situations,^{4,10} but no one seems to have determined clearly defined volume changes of hydrophobic interactions in non-equilibrium situations. Even though equilibrium volumes are of great interest, the important quantities in high pressure kinetics are activation volumes, which must be derived from pressure dependence of reaction rates.

The hydrolysis – aminolysis reaction of *p*-nitrophenyl esters with alkylamines has been reported to give striking rate increases with increasing alkyl chain length.^{5–9} The measurement of reaction rates of such reactions was found to be easily adapted to our high pressure equipment. From pressure studies of the reactions we have been able to deduce the activation volume associated with the interaction between a pair of CH_2 -groups.

EXPERIMENTAL

Equipment. The measurements were made with a Zeiss PMQ II spectrophotometer with an M4Q III monochromator at 400 nm. Signals were converted to the logarithmic scale and registered as extinction (optical density) on a Servograph REC 51 recorder. An optical high pressure cell constructed in this laboratory and described earlier,¹¹ was used. It could be filled and tightened in less than a minute, and pressure increased within seconds. The pressure transmitting fluid was Shell Tellus 17 oil. It served as a pressure reservoir in a large pressure

* Also at the Norwegian Underwater Institute, Gravdal, N-5034 Ytre Laksevåg, Norway.

vessel separated from the cell by a valve. The pressure was generated by an Enerpac hand pump, and read by a Budenberg gauge. The accuracy was ± 1 MPa at the highest pressures. All experiments were carried out at 25.0 ± 0.1 °C.

Chemicals. The *N*-alkylamines (pentyl, heptyl and nonyl) were purchased from Koch-light. They were dried with solid KOH for 24 h and distilled under nitrogen, heptyl- and nonylamine under reduced pressure. The first and last parts of the distillate were discarded. The purity was checked by GLC, with a Carbowax 20M-KOH, 1–1805, 3 m column. The gas chromatograph was an H.P. 5720A with a 3380 A integrator. The purities before use were: pentylamine, 99.35 %, b.p. 104.4 °C, heptylamine, 99.26 %, b.p. 156.9 °C, nonylamine, 99.27 %, b.p. 202.2 °C. The *p*-nitrophenyl esters (pentanoate and decanoate) were purchased from Sigma and used without further purification. Dioxan from Fluka AG was dried with solid NaOH and refluxed for several hours, decanted and further refluxed with freshly cut Na. It was distilled, and the first and last parts were discarded. Dioxan was used as solvent for the esters. Tris(hydroxymethyl)aminomethane–HCl buffer from Sigma was used as solvent for the amines. Its purity was 99.0–99.5 %. Distilled and ion-exchanged water was used throughout.

Methods. The amine solutions were made by dilution from stock solutions of high concentration. All solution were titrated with HCl to pH 9.00. Ionic strength was found to be unimportant. The esters were dissolved in dioxan to a concentration of about 0.25×10^{-2} M. 20 to 50 μ l of the ester solution were than added to 3 ml amine solution and brought into the pressure cell. There was no pH change during reaction. The concentration combinations were found by trial and error to give low reaction rates, for two reasons. First, the rates always increased by increasing pressure, and this could cause deflections in the curves at the highest pressures. It was necessary to obtain linear plots for at least ten minutes. Secondly, due to the time of filling and tightening of the cell and to allow temperature equilibration after the onset of pressure, we found the best reproducible results following 4–5 min after mixing.

THEORY

The reaction mechanism. The amine-catalyzed and water-catalyzed pathways of the aminolysis – hydrolysis of esters are well known. It is generally accepted that a tetrahedral intermediate is reversibly formed, and that an amine then can form a complex I, which may decompose to products.¹² This is a reaction of first order in amine

concentration, characterized by a rate constant k_1 . An encounter between the complex I and another amine forms a pair of ions, which also decomposes to products. This step is second order in amine concentration, and characterized by a rate constant k_2 . On the basis of these reactions schemes one obtains the relation (1) between reaction rate v and

$$v = [\text{ester}](k_0 + k_1[\text{RNH}_2] + k_2[\text{RNH}_2]^2) \quad (1)$$

reactant concentrations. This relation has also been experimentally confirmed.⁸

Buffer dissociation. The use of Tris tris(hydroxymethyl)aminomethane) as a buffer increases the reaction rate slightly because of catalysis. We use the definition (2) of a “hydrolysis” constant and when

$$k_0 = k_{\text{OH}^-}[\text{OH}^-] + k_{\text{T}}[\text{Tris}] \quad (2)$$

$[\text{OH}^-]$ and $[\text{Tris}]$ are constant, k_0 is also a constant. Other works have indicated that nucleophilic attack by water is negligible. The reason for choosing Tris buffer in this system is that the pressure dependence of pH then becomes negligible.¹² The ionization volume is near zero and the pH can be regarded as constant at all pressures, eqn. (3).

$$\left(\frac{\partial(\text{pH})}{\partial p}\right)_{\text{T}} = -\left(\frac{\partial \log[\text{H}^+]}{\partial p}\right)_{\text{T}} \approx 0 \quad (3)$$

However, the ionization constant of water, K_{w} is dependent on pressure, eqn. (4), with an ionization volume $\Delta V_{\text{w}} = -22.1 \text{ cm}^3 \text{ mol}^{-1}$. This leads to an increase of $[\text{OH}^-]$ as can be seen when eqn. (3) is inserted into eqn. (4) to give eqn. (5). Therefore, the

$$\begin{aligned} \left(\frac{\partial \ln K_{\text{w}}}{\partial p}\right)_{\text{T}} &= \left(\frac{\partial \ln[\text{H}^+]}{\partial p}\right)_{\text{T}} + \\ \left(\frac{\partial \ln[\text{OH}^-]}{\partial p}\right)_{\text{T}} &= -\frac{\Delta V_{\text{w}}}{RT} \end{aligned} \quad (4)$$

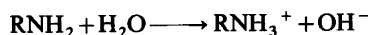
$$\begin{aligned} \left(\frac{\partial(\text{pOH})}{\partial p}\right)_{\text{T}} &= -\left(\frac{\partial \log[\text{OH}^-]}{\partial p}\right)_{\text{T}} = \\ \frac{\Delta V_{\text{w}}}{RT \ln 10} & \end{aligned} \quad (5)$$

hydrolysis constant k_0 will be pressure dependent for two reasons, eqn. (6), first, there is a pressure

$$\left(\frac{\partial \ln k_0}{\partial p}\right)_T = \left(\frac{\partial \ln k_{OH}}{\partial p}\right)_T + \left(\frac{\partial \ln [OH^-]}{\partial p}\right)_T + \left(\frac{\partial \ln k_T}{\partial p}\right)_T = \left(\frac{\partial \ln k_{OHT}}{\partial p}\right)_T + \left(\frac{\partial \ln [OH^-]}{\partial p}\right)_T \quad (6)$$

dependence of both single rate constants, which we have to combine into one, and then there is a pressure dependent hydroxyl ion concentration. Later, we will see that it is easy to correct for this. Anyway, it was considered simpler to work with a buffer with constant pH even if pOH varied, than to work with a buffer where both pH and pOH varied.

Amines at high pressure. It has been confirmed by other workers that only free amine is able to react with the esters.^{5,6} Amines in water ionize according to the scheme



with the ionization constant as given in eqn. (7).

$$K_b = [RNH_3^+][OH^-]/[RNH_2] \quad (7)$$

If the initial amine concentration was $[RNH_2]_0$, there will be a concentration $(1-x)[RNH_2]_0$ of free amine and a concentration $x[RNH_2]_0$ of proton ionized amine after ionization. The free amine concentration is then given by eqn. (8). Now, there is

$$[RNH_2] = (1 + K_b[H^+]/K_w)^{-1}[RNH_2]_0 \quad (8)$$

also a volume change ΔV_a associated with the ionization of an amine, determining the pressure dependence of the ionization constant, eqn. (9). The

$$K_b(p) = K_b^0 \exp(-p\Delta V_a/RT) \quad (9)$$

volume properties of aqueous solutions of primary amines have been investigated by Cabani *et al.*¹³ The volume changes in the proton ionization of amines have been found to be nearly independent of chain length, $\Delta V_a = 4.6 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$. We can then calculate the free amine concentration as a function of pressure p , eqn. (10).

$$[RNH_2](p) = [RNH_2]_0 \left[1 + \frac{K_b^0[H^+]}{K_w} \exp(-p(\Delta V_a - \Delta V_w)/RT) \right]^{-1} \quad (10)$$

Values of K_b^0 have been taken from Hoerr *et al.*¹⁴ and K_w^0 has been put equal to 10^{-14} .

Oakenfull⁸ showed that the dominating hydrophobic interaction occurred in the encounter between the complex I and an amine. This was especially prominent for long chain esters. Only in cases where the chain length exceeded a certain value, was the second order contribution to the rate observed. Unfortunately, for such long chain esters, micelle formation was inevitable at the concentrations necessary for observable rates.

Micelle formation. When the ester concentration $[E]$ increases above the critical micelle concentration M , the equilibrium (11) is attained,



where a number of m ester molecules (amphiphiles) E aggregate to a micelle E_m . The initial ester concentration is then given by eqn. (12).

$$[E]_0 = M + m[E_m] \quad (12)$$

When the amphiphiles go from the disperse to the micellar state, there is a molar volume change ΔV_m , so that the pressure dependence of M is as given in eqn. (13).

$$\left(\frac{\partial \ln M}{\partial p}\right)_T = -\frac{\Delta V_m}{RT} \quad (13)$$

There is not only a change in M with pressure, but also a change in aggregation number m .¹⁵ The aggregation number of nonionic amphiphiles seems to be reduced with pressure at the same time as the concentration of micelles increases correspondingly. The volume change accompanying the change in aggregation number is very pressure dependent, going from a positive value to zero as pressure increases.

A catalytic mechanism. Blyth and Knowles⁵ conclude from their investigations that the hydrolytic reaction does not appear to increase by the presence of amine. This may be perfectly true at one atmosphere. However, we suggest that an increased hydrolytic reaction catalyzed by amine may be important at higher pressures.

In that case, let E_m denote a single amphiphile or an ester micelle, and assume that a number n amines A can associate with E_m , eqn. (14).



With dissociation constant

$$K_a = \frac{[E_m][A]^n}{[E_m A_n]} \quad (15)$$

The total ester concentration is given by eqn. (16).

$$[E]_0 = M + m[E_m] + m[E_m A_n]. \quad (16)$$

We then assume that the ester can be hydrolyzed both in the normal way and in a catalyzed step, eqns. (17) and (18). Using eqns. (15) and (16), we can express this combined hydrolytic reaction rate by eqn. (19), where constant k_c is given by an expression similar to that of k_o , eqn. (2): eqn. (20), assuming a



$$\frac{d[P]}{dt} = ([E]_0 - M)[k_o + (k_c - k_o) \times \frac{[A]^n}{K_a + [A]^n}]m^{-1} \quad (19)$$

$$k_c = k_A [OH^-] + k_{TA}[Tris] \quad (20)$$

certain catalysis by the buffer also in this case. In the case of no micelle formation ($n=m=1$), eqn. (19) reduces to eqn. (21). The last term in this equation is

$$\frac{d[P]}{dt} = [E]_0(k_c + (k_c - k_o) \frac{[A]}{K_a + [A]}) \quad (21)$$

the catalytic contribution which shows a functional dependence of $[A]$ similar to an adsorption isotherm, *i.e.* at low $[A]$ (as compared to K_a) it is first order in $[A]$ and at high $[A]$ it is zero order. It must be assumed that all three constants, k_o , k_c and K_a are pressure dependent. The point is now that if K_a at one atmosphere is large compared to $[A]$, the catalytic contribution will not easily be observed. However, if the dissociation of $E_m A_n$, eqn. (14), is accompanied by a volume increase, the constant K_a will be reduced by increasing pressure. The K_a may be gradually comparable to the values of $[A]$, and the catalytic contribution more pronounced. This will lead to a curvature in the plot of reaction rate

versus $[A]$, for small $[A]$. In the case of micelles present, the over-all rate may be expressed by eqn. (22). More stringently, the micelle concentration is expressed by eqn. (23). As the aggregation number

$$v = ([E]_0 - M) \left\{ \left[k_o + (k_c - k_o) \frac{[A]^n}{K_a + [A]^n} \right] m^{-1} + k_1[A] + k_2[A]^2 \right\} \quad (22)$$

$$[E_m] = ([E]_0 - M \exp(-p\Delta V_m/RT))m(p)^{-1} \quad (23)$$

$m(p)$ decreases with pressure, the micelle concentration increases and may cause increased reaction rate. However, the reaction rate per micelle is dependent on the micelle size, *i.e.*, the number of amphiphiles $m(p)$ is believed to cancel, or at least to be without significant importance.

Activation volumes. From eqn. (24) we obtain, in the case of a first order, no micelle reaction ($m=n=1$, $k_c=0$, $K_a \gg [A]$), eqn. (24), and a plot of the rate v

$$v = [E]_0(k_o + k_1[A]) \quad (24)$$

versus $[A]$ yields k_o as an intercept and k_1 as a slope. Corresponding plots for higher pressure enable us to deduce the activation volumes associated with each constant, eqns. (25) and (26).

$$\Delta V_o^\ddagger = -RT \left(\frac{\partial \ln k_o}{\partial p} \right)_T \quad (25)$$

$$\Delta V_1^\ddagger = -RT \left(\frac{\partial \ln k_1}{\partial p} \right)_T \quad (26)$$

In the case of a first order reaction with catalysis ($m=n=1$, $k_c \neq 0$, $K_a \sim [A]$) the expression becomes as eqn. (27). At high $[A]$ ($K_a < [A]$), eqn. (27) reduces to eqn. (28). The extrapolation of this linearity to $[A]=0$ yields k_c as intercept, and we can find eqn. (29).

$$v = [E]_0 \left\{ \left[k_o + (k_c - k_o) \frac{[A]}{K_a + [A]} \right] + k_1[A] \right\} \quad (27)$$

$$v \approx [E]_0(k_c + k_1[A]) \quad (28)$$

$$\Delta V_c^\ddagger = -RT \left(\frac{\partial \ln k_c}{\partial p} \right)_T \quad (29)$$

At the same conditions for a second order reaction the expression for the rate is given by eqn. (30). Rearrangement yields eqn. (31) and k_1 and k_2 can be found as before. Accordingly, ΔV_2^\ddagger is given by eqn. (32). We have not found it necessary to use n , m or K_a explicitly. Our model is thus confined to the use of k_o , k_c , k_1 , k_2 and their pressure derivatives.

$$v \approx [E]_o(k_c + k_1[A] + k_2[A]^2) \quad (30)$$

$$\frac{\frac{v}{[E]_o} - k_c}{[A]} = k_1 + k_2[A] \quad (31)$$

$$\Delta V_2^\ddagger = -RT \left(\frac{\partial \ln k_2}{\partial p} \right)_T \quad (32)$$

Treatment of data. By means of a computer program, free amine concentrations at all pressures were calculated from eqn. (10), and ester concentration from eqn. (23). With the observed rates as input, the constants k_o , k_c , k_1 and k_2 were calculated at all pressures by means of a least square procedure. The results were again subjected to a least square procedure, so that ΔV_i^\ddagger 's could be found from the linear pressure dependence of the constants. ΔV_0^\ddagger was considered to be associated with the pure hydroxyl-ion hydrolysis, *i.e.* without any contribution from other parts of the ester molecule. In other words, ΔV_0^\ddagger was regarded as characteristic of the breakage of an ester linkage.

ΔV_c^\ddagger has a similar interpretation, but was also

considered to involve side effects due to the associated amine(s). ΔV_1^\ddagger was considered to arise in the activation process following the contact between the ester and an amine. We believe it to consist of two contributions, although these may not be wholly independent: eqn. (33). ΔV_{c1}^\ddagger is a constant characteristic of the type of chain interaction (short-

$$\Delta V_1^\ddagger = \Delta V_{c1}^\ddagger + n\Delta V_{g1}^\ddagger \quad (33)$$

$$\Delta V_2^\ddagger = \Delta V_{c2}^\ddagger + n\Delta V_{g2}^\ddagger \quad (34)$$

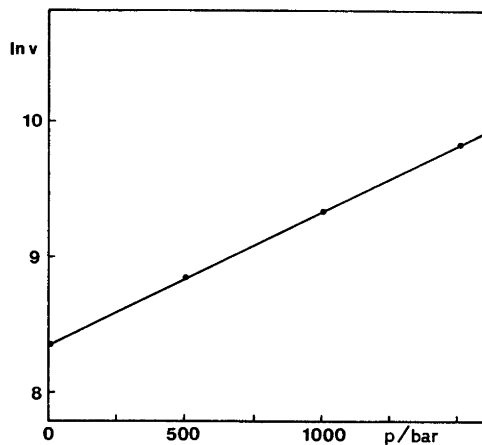


Fig. 1. The pressure dependence of the buffer hydrolysis rate of *p*-nitrophenylpentanoate. [ester] = 0.207×10^{-4} M, pH = 9.00, $T = 298$ K.

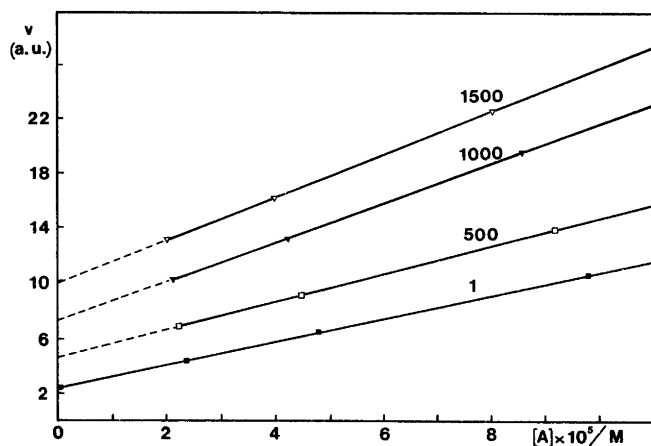


Fig. 2. The hydrolysis-aminolysis rate (arbitrary units) of pentanoate ester as function of pentylamine concentration at various pressures (in bar). [ester] = 0.359×10^{-4} M, pH = 9.00, $T = 298$ K.

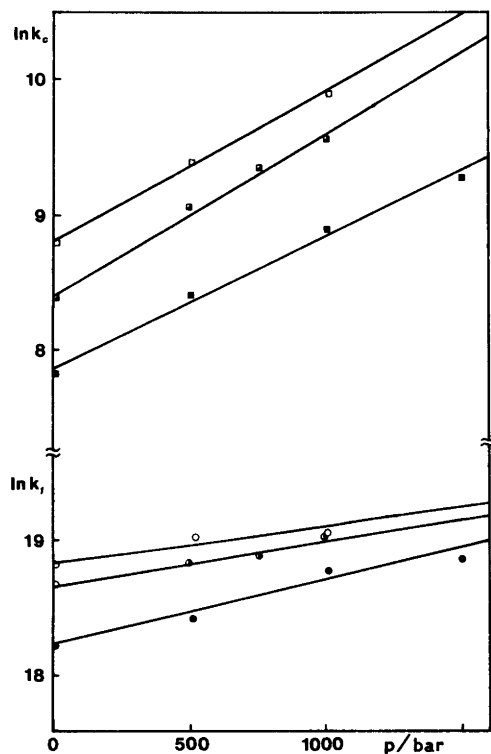


Fig. 3. The pressure dependence of the catalytic and the first order rate constants in the reaction between pentanoate ester and pentylamine (■●), heptylamine (▣●) and nonylamine (□○).

short, short-long or long-long) involved, while ΔV_{g1}^{\ddagger} is a group increment per pair of CH_2 -groups in contact and n is the number of pairs.

ΔV_2^{\ddagger} was similarly considered to arise in the activation process following the contact between the intermediate I and amine. In the same way as ΔV_1^{\ddagger} , it was split into two contributions, eqn. (34), with obvious notation.

RESULTS

We have measured the rate changes with pressure for six combinations of esters and amines. The esters are *p*-nitrophenylpentanoate and *p*-nitrophenyldecanoate, and the amines are pentyl, heptyl and nonyl *n*-amines. In Fig. 1, a plot is made of the pressure dependence of the hydrolysis rate of *p*-nitrophenylpentanoate by pure buffer at pH 9.00. From the slope of the curve, the activation volume for the hydroxyl ion hydrolysis could be calculated to $\Delta V_0^{\ddagger} = -24.5 \text{ cm}^3 \text{ mol}^{-1}$. In Fig. 2, plots are made of the hydrolysis-aminolysis rate of the pentanoate by pentylamine as functions of $[A]$, at several pressures. Extrapolations to $[A]=0$ yield values of k_c , and slopes yield values of k_1 , according to eqn. (28). These two constants are shown as functions of pressure in Fig. 3. From this, ΔV_c^{\ddagger} and ΔV_1^{\ddagger} are found. In Fig. 4, plots are made of the corresponding rates between pentanoate and heptylamine as functions of $[A]$, at several

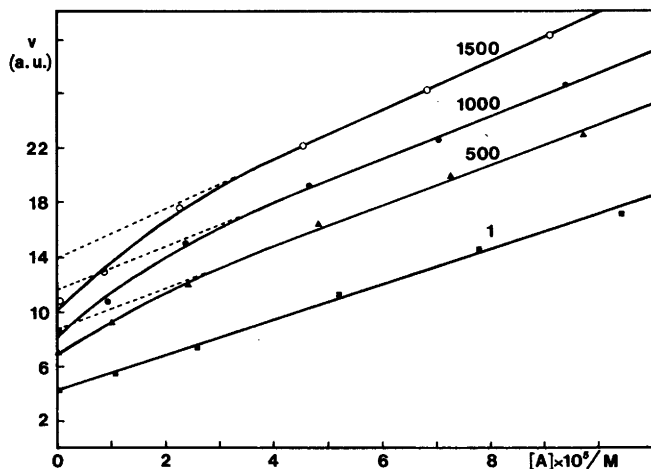


Fig. 4. The hydrolysis-aminolysis rate (arbitrary units) of pentanoate ester as function of heptylamine concentration at various pressures (in bar). $[\text{ester}] = 0.207 \times 10^{-4} \text{ M}$, $\text{pH} = 9.00$, $T = 298 \text{ K}$.

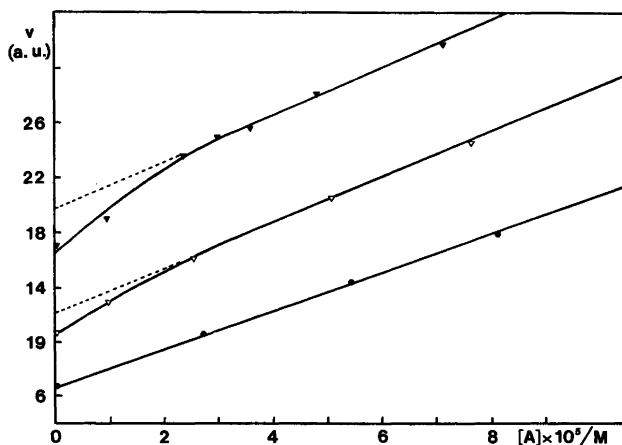


Fig. 5. The hydrolysis-aminolysis rate (arbitrary units) of pentanoate ester as function of nonylamine concentration at various pressures (in bar). $[\text{ester}] = 0.310 \times 10^{-4} \text{ M}$, $\text{pH} = 9.00$, $T = 298 \text{ K}$.

pressures. Here, the curvatures for small $[A]$ are shown to be significant. Again, from the intercepts found by extrapolation and the slopes, the pressure dependence of k_c and k_1 are given in Fig. 3.

In Fig. 5, equivalent plots are made for nonylamine at various pressures. The curvatures are also here clearly seen. The pressure dependence of k_c and k_1 for the nonylamine reaction can be seen in Fig. 3.

In Fig. 6, plots are made of the reaction rate for the hydrolysis-aminolysis of decanoate ester by pentylamine as function of $[A]$, at several pressures. All corrections are included and the plots are made

according to eqn. (28). In this case the decanoate molecules aggregate to micelles, but still there is no second order contribution. Slopes and intercepts, given as k_1 and k_c are shown as functions of pressure in Fig. 7.

Finally, in the reaction between decanoate and heptylamine, a second order contribution is observed. This can be seen in Fig. 8, where the rates are plotted *versus* $[A]$, at several pressures. In Fig. 9, the plots from Fig. 8 are linearized according to eqn. (31). From these curves, the three constants k_c , k_1 and k_2 could be evaluated, and they are shown in Fig. 7 as functions of pressure.

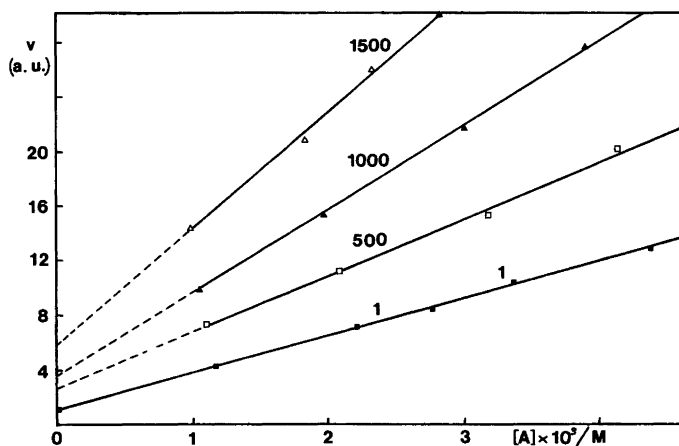


Fig. 6. The hydrolysis-aminolysis rate (arbitrary units) of decanoate ester as function of pentylamine concentration at various pressures (in bar). $[\text{ester}] = 0.291 \times 10^{-4} \text{ M}$, $\text{pH} = 9.00$, $T = 298 \text{ K}$.

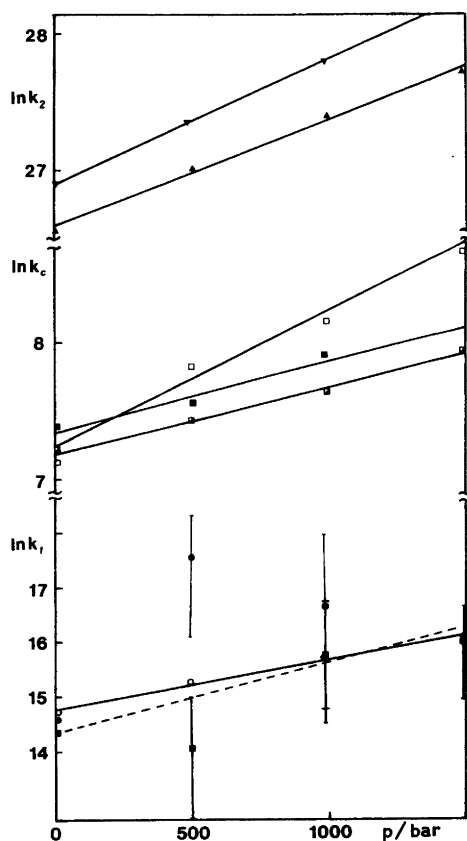


Fig. 7. The pressure dependence of the catalytic, first and second order rate constants in the reaction between decanoate ester and pentylamine (\square , \circ), heptylamine (\blacksquare , \blacktriangle) and nonylamine (\bullet , \blacktriangledown).

A second order contribution was also observed in the reaction between decanoate and nonylamine. The rates are plotted *versus* $[A]$ at some pressures in Fig. 10, after linearization according to eqn. (31). The functional dependence of the constants k_c , k_1 and k_2 on pressure can be seen in Fig. 7. As the constant k_c could not be obtained experimentally at $[A]=0$, its value had to be estimated in the case of the curved plots, Fig. 8 and correspondingly for the nonylamine case. The linearization of the second order plots include these estimated values. Because of the uncertainty in k_c and because the rates and rate differences obtained from the linear extrapolations (Figs. 9 and 10) are very small, their relative uncertainties become rather large. This is evident from the plots of k_1 *versus* pressure, Fig. 7. An interesting observation is that while the activation volumes ΔV_0^\ddagger found in the cases of pentanoate hydrolysis have values about $-25 \text{ cm}^3 \text{ mol}^{-1}$, the ΔV_0^\ddagger -values for decanoate hydrolysis are zero. The set of activation volumes obtained from the experimental data are given in Table 1.

DISCUSSION

There has been some earlier works on alkaline ester hydrolysis under pressure. Studies of aliphatic esters of the lower fatty acids have given activation volumes of about -5 to $-10 \text{ cm}^3 \text{ mol}^{-1}$.^{16,17} To our knowledge, volume changes for base-catalyzed hydrolysis of *p*-nitrophenyl esters have only been studied by Neuman Jr. *et al.*,¹² who found the values -3 and $-4 \text{ cm}^3 \text{ mol}^{-1}$ for the acetate and propionate, respectively.

Table 1. Activation volumes as calculated from the pressure dependence of the kinetic constants k_0 , k_c , k_1 and k_2 .

	Buffer	Pentylamine	Heptylamine	Nonylamine
Pentanoate ester				
ΔV_0^\ddagger	-24.5 ± 1			
ΔV_c^\ddagger		-23 ± 2	-29 ± 3	-27 ± 1
ΔV_1^\ddagger		-11 ± 2	-8 ± 1	-5 ± 1
Decanoate ester				
ΔV_0^\ddagger	0 ± 2			
ΔV_c^\ddagger		-24 ± 3	-12 ± 6	-12 ± 5
ΔV_1^\ddagger		-20 ± 1	-35 ± 15	-70 ± 30
ΔV_2^\ddagger			-19 ± 2	-18 ± 2

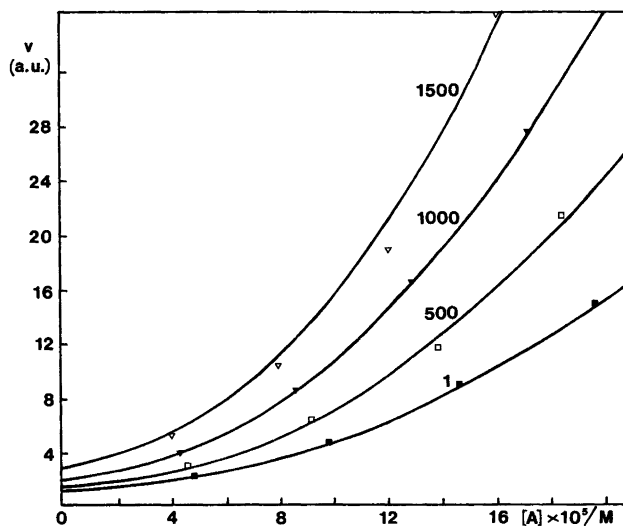


Fig. 8. The hydrolysis-aminolysis rate (arbitrary units) of decanoate ester as function of heptylamine concentration at various pressures (in bar). [ester] = 0.291×10^{-4} M, pH = 9.00, $T = 298$ K.

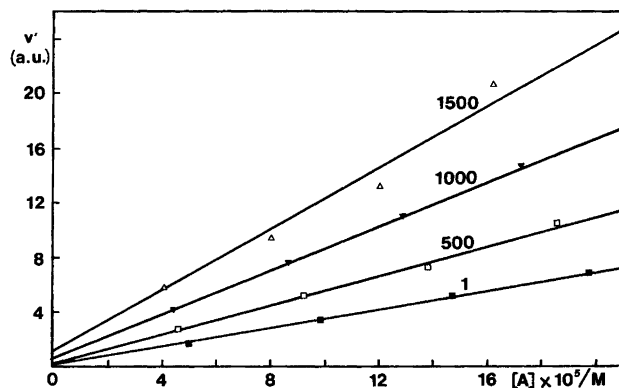


Fig. 9. Linearized rate function of the data from the preceding figure.

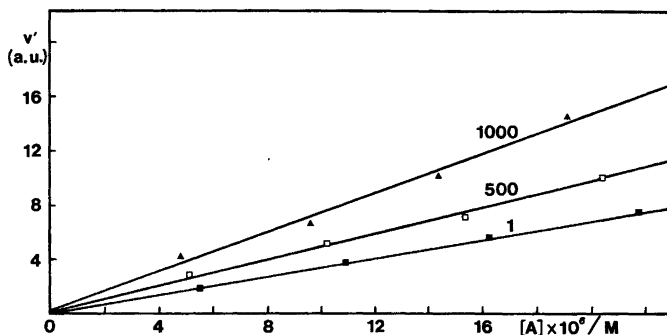


Fig. 10. Linearized rate function of the data from the reaction between decanoate ester and nonylamine. [ester] = 0.291×10^{-4} M, pH = 9.00, $T = 298$ K.

From eqn. (6) it turns out that our observed volume change ΔV_0^* is the result of two contributions; first the hydrolysis volume change itself, ΔV_h^* , and then the ionization volume of water, ΔV_w^* , eqn. (35). Inserting the average value for all our

$$\Delta V_0^* = \Delta V_h^* + \Delta V_w^* \quad (35)$$

ΔV_0^* s, $\overline{\Delta V_0^*} = -24.5 \text{ cm}^3 \text{ mol}^{-1}$ and the value of $\Delta V_w^* = -22.1$, we obtain $\Delta V_h^* = -2.4 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$. This is in fair agreement with the values found by Neuman Jr. *et al.*¹² (We are indebted to Prof. R. C. Neuman, Jr. for discussions on this point). The reason for a zero volume change in the cases of decanoate hydrolysis is not known. Since the volume change of cleavage of an ester linkage is believed to be of the same order of magnitude for most esters, the only explanation must be that some other volume change of opposite sign occurs simultaneously. It seems that all our curves of rates *versus* amine concentration, both first order and second order, show a positive initial curvature. This can be explained by a catalytic mechanism as sketched in the theory section. k_c may be found from the linear curves by simple extrapolation. Within this framework the second order curves are assumed to have an inverted s-shape, so that a parabolic extrapolation into $[A] = 0$ yields k_c . We have not confirmed this hypothesis in any other way, but we find it suitable to cover experimental observations. Although much work on micellar catalysis has been carried out,¹⁸ we have not found information of relevance to the case where the micelle itself consists of the catalyzed molecules. We have, however, applied the same formalism in the micellar cases as in the non-micellar cases, *i.e.* eqn. (22). As to the further mechanistic details of the overall hydrolysis process in these cases, Blyth and Knowles⁵ assumed a mechanism without the second order term in amine. Oakenfull⁸ included the second order term as the most important factor in the interpretation of his results. Blyth and Knowles⁵ used carbonate–bicarbonate buffer and found a large rate dependence on buffer molarity, while Oakenfull⁸ found it necessary to use borate and imidazole buffer and found no detectable catalysis. We have used Tris buffer, as did Neuman Jr.,¹² who also found that catalysis was clearly indicated. Ionic strength, according to our measurements, does not influence the rate significantly either at high or low pressures. pH has an indirect influence through its

control of the present free amine concentration. Contrary to the results found by Guthrie,¹⁹ the total rate in our experiments increased with increasing micelle concentration. In the case of pentylamine it was necessary to use a rather high amine concentration to achieve an acceptable rate. It is possible that the chain of the amine must penetrate into the micelle to be able to react, and this may be more difficult for a short amine chain. As to the volume changes involving the short chain ester, we would have expected almost the same activation volume ΔV_1^* for all three amines. All amines have longer chains than the ester, and any kind of contact should limit the number of CH_2 -groups in contact to the number of the ester chain. Nevertheless, from Table 1 there seems to be a slight, although significant increase in ΔV_1^* for increasing chain length. This may be due to the possibility of interaction of the amine with a larger part of the ester than just the chain. The observed volume change is an average quantity and may include other contributions. In a way, this is implied in the relations (33) and (34), by means of the constant ΔV_{ci}^* .

The results from our partitioning of the volume changes are the following:

$$\Delta V_{c1}^* = -18.5 \text{ cm}^3 \text{ mol}^{-1}, \Delta V_{g1}^* = 0.5 \text{ cm}^3 \text{ mol}^{-1}$$

$$\Delta V_{c2}^* = -22.5 \text{ cm}^3 \text{ mol}^{-1}, \Delta V_{g2}^* = 0.5 \text{ cm}^3 \text{ mol}^{-1}$$

The first values are for the pentanoate interactions, the next values are for the amine–amine interactions. Uncertainties are here of the order of $1 \text{ cm}^3 \text{ mol}^{-1}$ for the ΔV_{gi}^* and $3 \text{ cm}^3 \text{ mol}^{-1}$ for the ΔV_{ci}^* . Values for the decanoate interactions are not considered, due to the large uncertainties. The presented values are in good agreement with each other, although different mechanisms are apparently involved. Earlier results obtained at one atmosphere indicated that only second order effects involved hydrophobic interactions, but it is, of course, conceivable that comparable interactions also appear in the ester–amine contact. The question is where these interactions influence a rate-determining step. The result then indicates that the activation volumes resulting from contact between a pair of CH_2 -groups are small and positive.

REFERENCES

1. Asano, T. and LeNoble, W. *J. Chem. Rev.* 78 (1978) 407.
2. Hamann, S. D. In Conway, B. E. and Bockris, J. O. M., Eds., *Modern Aspects of Electrochemistry*, Plenum, New York 1974, Vol. 9.
3. Terasawa, S., Itsuki, H. and Arakawa, S. *J. Phys. Chem.* 79 (1975) 2345.
4. Ben-Naim, A. *Hydrophobic Interactions*, Plenum, New York 1980.
5. Blyth, C. A. and Knowles, J. R. *J. Am. Chem. Soc.* 93 (1971) 3017.
6. Blyth, C. A. and Knowles, J. R. *J. Am. Chem. Soc.* 93 (1971) 3021.
7. Oakenfull, D. G. *J. Chem. Soc. Chem. Commun.* (1970) 1655.
8. Oakenfull, D. G. *J. Chem. Soc. Perkin Trans. 2* (1973) 1006.
9. Oakenfull, D. G. and Fenwick, D. E. *Aust. J. Chem.* 27 (1974) 2149.
10. Morild, E. *Acta Chem. Scand. A* 34 (1980) 777.
11. Morild, E. and Tvedt, I. *Acta Chem. Scand. B* 32 (1978) 5.
12. Neuman, R. C., Jr., Lockyer, G. D., Jr. and Martin, J. J. *J. Am. Chem. Soc.* 98 (1976) 6975.
13. Cabani, S., Conti, G. and Lepori, J. *J. Phys. Chem.* 78 (1974) 1030.
14. Hoerr, C. W., McCorkle, M. R. and Ralston, A. *W. J. Am. Chem. Soc.* 65 (1943) 328.
15. Nishikido, N., Shinozaki, M., Sugihora, G., Tanaka, M. and Kaneshina, S. *J. Colloid Interface Sci.* 74 (1980) 474.
16. Andersen, B., Grønlund, F. and Olsen, J. *Acta Chem. Scand.* 23 (1969) 2458.
17. Tonnet, M. L. and Whalley, E. *Can. J. Chem.* 53 (1975) 3414.
18. Sudhölter, E. J. R., VdLangkruis, G. B. and Engberts, J. B. F. N. *Recueil* 99 (1980) 73.
19. Guthrie, J. P. *J. Chem. Soc. Chem. Commun.* (1972) 897.

Received September 9, 1980.