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Utrecht, Netherlands

Kinetics of the Acid Hydrolysis of Cyclic Oligomers from Nylon 6 and Nylon 6.6

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SUMMARY:

A kinetic investigation is offered of the hydrolysis in 7.72 N aqueous hydrochlorie acid at 110° C. of the cyclic di-, tri- und tetraamides of ε-caprolactam and of the cyclic diamide from hexamethylene diamine and adipic acid. The intermediates of the reaction, identified by chromatography, provide definite proof of the constitution of these cyclic compounds.

For the remarkable difference between the rate constants of the two isomeric cyclic diamides no simple explanation could be given on known structural grounds.

ZUSAMMENFASSUNG:

Die Hydrolyse in 7.72 N Salzsäure bei 110°C. der cyclischen Di-, Tri und Tetraamide des ε-Caprolactames und des cyclischen Diamides aus Hexamethylendiamin und Adipinsäure wird kinetisch untersucht. Die bei der Reaktion auftretenden Zwischenprodukte wurden auf chromatographischem Wege identifiziert und beweisen die Konstitution der betreffenden cyclischen Verbindungen.

Für den auffallenden Unterschied in der Hydrolysegeschwindigkeit der beiden isomeren cyclischen Diamide konnte auf Grund bekannter Strukturprinzipien keine einfache Erklärung gegeben werden.

1 *Introduction*

In two brief preliminary communications, the essential results of an investigation on the acid hydrolysis of three cyclic oligomers of ε-caprolactam isolated from technical Nylon 6 polymerisates¹) and of a cyclic oligoamide isolated from Nylon 6.6 have been published previously²).

Through identification by a paper chromatographic technique of the intermediate products formed during hydrolysis, the molecular size of the substances in question could be established beyond doubt. The results confirmed the molecular weight determinations by cryoscopy carried out by I. and M. Rothe³).

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*) Communication Nr. 96 from the Institute for Cellulose Research of the AKU and affiliated Companies, Utrecht, Netherlands.

¹) P. H. Hermans, Recueil Trav. chim. Pays-Bas **72** (1953) 798.

²) P. H. Hermans, Nature [London] **177** (1956) 126–128.

³) I. Rothe and M. Rothe, Chem. Ber. **88** (1955) 284.

As the chromatographic technique employed allowed an approximately quantitative determination of the linear oligomers produced as intermediates in the hydrolysis of the cyclic polyamides, and as series of successive first order reactions are involved which can be easily treated theoretically, approximate values of the rate constants for the hydrolysis of the amide bonds in the ring systems investigated and in linear molecules could be also estimated by kinetic analysis.

In the present paper a more detailed account of this analysis will be given along with additional experiments based on more accurate analytical procedures and aiming at establishing more reliable values of some of the rate constants in question. Such work seemed to be justified in view of the very remarkable differences in rate of hydrolysis as found in this preliminary investigation, indicating, for instance, a more than twelvefold difference between the Nylon 6 cyclic dimer and its isomer, the cyclic diamide from Nylon 6.6.

In the preliminary as well as in the present work it has been assumed that the rate of hydrolysis of the amide bond in *linear* oligomers is independent of molecular size. Meanwhile this assumption has been corroborated experimentally by other work from this laboratory through a kinetic analysis of the rate of hydrolysis of the synthetically prepared linear dimer and trimer and of mixtures of higher oligomer chains[4]) in the Nylon 6 series.

According to the second paper quoted in ref. 4, the best value of the rate constant in question, under the standardized conditions of concentration and temperature as used throughout all this work, is 0.36 h^{-1} (not far off the value of 0.34 arrived at in the preliminary investigation).

Section 2 of the present paper is concerned with the origin of the substances investigated and section 3 with the experimental techniques employed.

In section 4 are given the mathematical equations applied in the kinetic analysis and in section 5 the experimental results along with the rate constants derived therefrom.

In section 6 the results are discussed.

2 *Materials*

In the purity control of the cyclic Nylon 6 oligomers employed, the experience gained in working out a procedure for their quantitative separation[5]), was used. The various substances will be designated by roman figures.

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[4]) D. Heikens, J. Polymer Sci. **22** (1956) 65; D. Heikens, J. Polymer Sci., in press.

[5]) D. Heikens, Recueil Trav. chim. Pays-Bas **75** (1956) 1199.

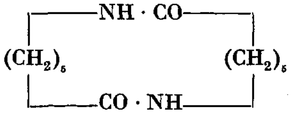
I Cyclic dimer of ε-caprolactam (m.p. 347°–348° corr.) was isolated from a technical sublimate obtained upon subjecting a large quantity of molten polymer to vacuum treatment and was purified by recrystallization from water. Through hydrolysis it could be converted into the theoretical quantity of ε-aminocaproic acid.

II Cyclic trimer of ε-caprolactam (m.p. 247–248° corr.), was isolated from the most water soluble fraction of an aqueous extract of polymer and purified by repeated fractional crystallization[1]). As disclosed by the fractional sublimation technique described in ref. 5, it contained a small percentage of cyclic dimer.

III Cyclic tetramer of ε-caprolactam as obtained in certain technical investigations was received in essentially pure form from German colleagues (m.p. 241–242° corr.).

IV A sample of a cyclic diamide isolated from Nylon 6.6 was obtained by courtesy of Dr. J. W. Reynolds (Manchester). This substance contains one residue of adipic acid and one of hexamethylene diamine per molecule and has no endgroups. It is isomeric with the cyclic dimer of Nylon 6.

Formula of the substances used:



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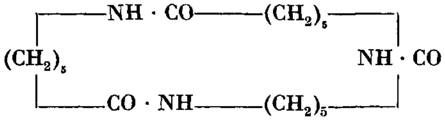

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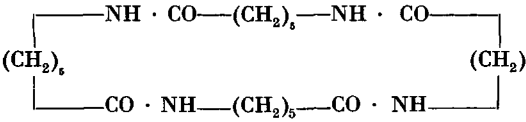

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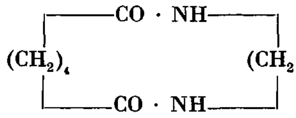

IV

3 *Experimental techniques*

3.1 *Hydrolysis conditions*

All hydrolysis experiments were carried out in aqueous 7.72 N (25 per cent of weight) hydrochloric acid solution using always concentrations between 50–60 mg./ml.

Quantities of the solution adopted to the requirements of the technique of analysis to follow were sealed into a Pyrex glass tube and heated at 110°C. for different time intervals.

In the hydrolysis experiments of the cyclic dimer (I) and of the cyclic diamide of Nylon 6.6 (IV) in which more precise methods were applied the temperature was kept at precisely 110°C. (± 0.4°C.) in order to achieve comparability with hydrolysis experiments of linear oligomers[4]). The analytical procedures for the different substances will be dealt with separately below.

3.2 *Analysis of hydrolyzates of cyclic dimer (I)*

Upon hydrolysis of I, there is first produced the linear dimer of ε-aminocaproic acid (ACA), which is subsequently hydrolyzed into two molecules of ACA.

Three different series of measurements were performed. In the first was followed the change in concentration of I and in the second the sum of the concentrations of linear dimer and ACA was determined by end group titration. In the third series linear dimer and ACA were both estimated by chromatographic analysis.

3.2.1. *Determination of unreacted I*

The reaction product was transferred into a 100 ml. round bottom flask using a methanol rinse. In order to remove the larger part of hydrochloric acid and methanol, the flask was evacuated (25 mm mercury) and heated at 35 °C. in an airbath while kept turning slowly around its length axis. A small current of air through a capillary inlet tube shortened the drying period. The drying procedure was identical with that earlier described for linear oligomers[4]).

The dried product was dissolved in 20 ml. ethanol and the solution passed through a column loaded with 4 g. Dowex-2 anion exchange resin in the hydroxyl-state swollen in ethanol. After eluting with another 40 ml. of ethanol the total effluent, received in a tarred 100 ml. roundbottom, was subjected to destillation. A final residue of about 10 ml. was evaporated in vacuo at room temperature. After heating for 3 hrs. at 100 °C. the weight of the recovered cyclic dimer was determined. (Correction for blank of the column procedure amounted to only 0.5 mg.).

Results of these experiments are presented in Fig. 1 as black dots.

As later experiments concerned with end group determination (see next section) indicated that in contact with 25% HCl and methanol ACA possibly may become esterified in part while there was no guarantee that amino acid esters are quantitatively hydrolysed by the alkaline resin, the experiments were repeated omitting the methanol rinse (using hydrochloric acid in substitution). Also the hydrolysate was evaporated at room temperature in vacuo over solid potassium hydroxide.

Furthermore, to make sure that possible partial esterification did not interfere upon dissolution of the dried residue in ethanol, there was added in 4 out of 8 experiments 10 per cent of ammonia to the solution prior to its passage over the column.

In Fig. 1 the original experiments with methanol rinse are represented by dots, the experiments with and withouth addition of ammonia by plus signs and crosses respectively. They are all mutually consistent and are evaluated together.

3.2.2 *Determination of the sum of the linear products*

The sum of the NH_2- and CO_2H-groups of ACA and its linear dimer were determined by potentiometric titration in benzylalcohol as described in ref. 4.

In the first experiments where the hydrolysate was evaporated in the presence of methanol at 35 °C. as described under 3.2.1 and in ref. 4, erratic results were obtained.

One of us (VELDHOVEN) found that ACA when subjected to this procedure suffered a loss of end groups in an uncontrollable measure whereas correct results were obtained if the use of methanol was avoided. The drying was therefore performed in the rotating flask (35 °C., 25 mm) without the use of CH_3OH and alternatively in vacuo over KOH. The results all represented in Fig. 2 did not show systematic differences.

3.2.3 *Chromatographic estimation of individual linear oligomers* (see also [6]))

Small known quantities of cyclic dimer were hydrolyzed for different reaction times. The reaction product was transferred to glass dishes by rinsing with water and the obtained solutions were subjected to rapid evaporation at about 80 °C. Practically no hydrolysis

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[6]) P. H. HERMANS, D. HEIKENS, and P. F. VAN VELDEN, J. Polymer Sci. **16** (1955) 451.

occurs at this temperature. The dry residues were kept in an oven at 110°C. for 2 hrs. (to remove excess HCl) and then dissolved in a measured quantity of water containing a drop of methyl orange. Just enough powdered $NaHCO_3$ was added to neutralize the HCl-salts of the amino acids.

Then 5 and (or) 10 μl of the solution spotted on a large sheet of Whatman No. 1 paper, along with spots of standard solutions of ACA of increasing concentration were subjected to ascending elution with aqueous n-propanol of spec. grav. 0.813. After drying at room temperature, the paper sheet was sprayed with a 0.1% solution of ninhydrin in n-butanol and the colour was developed in a stove at 110°C. during 5 minutes. The concentrations of the spots were estimated by visual comparison with the spots from the standard ACA-solution. Some preliminary experiments with solutions of pure linear oligomers together with standard ACA solutions showed that the estimated concentrations correspond with molar concentrations.

The results for ACA and its linear dimer are presented in Fig. 1 as open squares and triangles respectively.

3.3 *Analysis of hydrolyzates of the cyclic trimer (II)*

The course of the concentrations of the linear trimer and dimer with time was followed by the chromatographic technique as described under 3.2.3. The results are given in Fig. 3.

3.4 *Analysis of hydrolyzates of the cyclic tetramer (III)*

Here the linear tetra-, tri- and dimer were estimated chromatographically in the same way. The results are presented in Fig. 4. Owing to the slight solubility of the linear tetramer in water it is felt that the time of its maximum concentration is more reliable than its concentration which may have been estimated considerably too low.

3.5 *Analysis of hydrolyzates of the cyclic diamide of Nylon 66 (IV)*

In the first step of the hydrolysis a linear amide containing one residue of adipic acid and one of hexamethylene diamine is formed. In one series of experiments this substance was estimated chromatographically (3.5.1).

The second step is the hydrolysis of this linear amide into adipic acid and hexamethylene diamine. In a separate series the latter substance was determined by volumetric titration (3.5.2).

3.5.1 *Chromatographic estimation of the linear amide*

The linear amide was determined in exactly the same way as the linear amide produced by hydrolysis of the isomeric cyclic dimer of Nylon 6. Both linear amides have the same R_f-value and in analogy to well established experience concerning the other linear products, it was assumed that the concentration determined for the Nylon 6.6 dimer is a molar one. The results are given in Fig. 5 (open circles).

3.5.2 *Determination of hexamethylene diamine*

Sealed off samples of 2 ml. of a 6% solution of the Nylon 6.6 cyclic diamide in 7.72 N HCl were heated for various times.

The reaction product was passed through a column of size 350× 18 mm. containing 30 g. (conditioned weight) of Dowex-2 anion-exchange resin in the hydroxide form. The column was eluted with 350 ml. distilled water and the total effluent was received in excess 0.1 N aqueous HCl. The only ionic compound passing the column, hexamethylene diamine, was determined by titration with 0.1 N KOH with bromo cresol purple as an indicator.

Preliminary experiments showed that the conversion in the column was not exactly 100 per cent, depending on the concentration of the hexamethylene diamine.

A standardization procedure with Nylon 6.6 salt was used to obtain data accurate within 2 per cent for the larger and about 5 per cent for the lower concentration. The reproducibility of the procedure was good.

The results are presented in Fig. 5 (triangles).

4 *Theoretical part*

4.1 *Introduction*

The hydrolysis in the presence of an excess of concentrated hydrochloric acid of a cyclic amide and its intermediate hydrolysis products, the linear amides, is assumed to follow a first order course. The experimental results have confirmed this assumption. As at large reaction times the cyclic amides are totally converted into monomeric residues, the concentrations of the linear oligoamides will go through a maximum value.

The hydrolysis of any cyclic n-amide will be described by a rate constant k_n being the average of the constants of the n-amide bonds which are not necessarily equal to each other.

The hydrolysis of the linear oligoamides of Nylon 6 can be described with one rate constant k, independent of chain length[4]). It is assumed that the same rate constant holds also for the linear monoamide produced as an intermediate in the hydrolysis of the Nylon 6.6 cyclic diamide.

The symbols used in the chemical and mathematical equations and in the presentations of the experimental results are given in the following table.

Table 1. List of symbols

Substance	Symbol	Fractions of Residues	Average rate constants per amide bond	Time of maximum concentration
(I) cyclic dimer of Nylon 6	X_2	x_2	k_2	–
(II) cyclic trimer of Nylon 6	X_3	x_3	k_3	–
(III) cyclic tetramer of Nylon 6	X_4	x_4	k_4	–
(IV) cyclic diamide of Nylon 6.6	X_2^*	x_2^*	k_2^*	–
linear n-mers of Nylon 6	U_n	u_n	k	$t_m(u_n)$

The equations of the reactions occurring in the hydrolysis of the substances investigated are given below together with the differential equations.

In the *reaction* equations, the relevant rate constant pertaining to one amide bond is printed on top of the arrow along with a coefficient equal to the number of amide bonds participating in the reaction under consideration.

In the following we shall designate as "residues" the components of the amides which appear separated after complete hydrolysis.

Cyclic substances composed of *m* residues will be given the symbol X_m and linear products composed of *n* residues the symbol U_n.

In the differential equations and their solutions x_m and u_n will represent the quantity of X_m and U_n at any time t during hydrolysis, expressed as the fractional number of residues present in that form compared to the number of units originally present in the quantity of the particular cyclic amide X_m $(m \geqslant n)$ from which the reaction was started at the time $t = 0$.

Thus, if $x'_{m,o}$ equals the *number of molecules* of the cyclic m-mer at $t = 0$ and x'_m and u'_n are the *number of molecules* of cyclic m-mer and of linear n-mer at $t = t$ then

$$x_m = x'_m / x'_{m,0}$$

$$u_n = nu'_n / mx'_{m,0}$$

Thus, the coefficient of any term in a differential equation for $du_m/dt = \dot{u}_m$ describing the formation of U_i out of U_n,

$$U_n \xrightarrow{ak} U_i + U_j$$

is found by multiplication of *two* factors.

The *first* factor is: *ak*, where *a* is the number of amide bonds in U_n capable of reacting to produce U_i. The *second* factor is in^{-1}, which equals the fraction of residues, which a i-mer molecule receives out of a n-mer molecule in each reaction step.

Thus the contribution to $du_i/dt = \dot{u}_i$ from the reaction in question is given by

$$\dot{u}_i = ai\, n^{-1}\, ku_n$$

Evidently, the equation describing the change in the concentration of U_n-residues is equal to $(m = n)$

$$-\dot{u}_n = a\, k\, u_n$$

4.2 *Equations*

Cyclic dimer I

Reactions:	Differential equations:
$X_2 \xrightarrow{2k_2} U_2$	$\dot{x}_2 = -2k_2x_2$
$U_2 \xrightarrow{k} 2U_1$	$\dot{u}_2 = 2k_2x_2 - ku_2$

Solutions are:

$$x_2 = \exp\,[-2k_2\,t]$$

$$u_2 = 2k_2(k-2k_2)^{-1}\left\{\exp\,[-2k_2t] - \exp\,[-kt]\right\}$$

$$u_1 = 1 - x_2 - u_2$$

$$t_m(u_2) = (k-2k_2)^{-1}\ln\,(k/2k_2)$$

Cyclic diamide IV

In the case of the cyclic diamide of Nylon 6.6 the same formula can be used except that u_1 now represents the sum of the fractions of residues present in hexamethylene diamine and adipic acid.

Cyclic trimer II

Reactions:	Differential equations:
$X_3 \xrightarrow{3k_3} U_3$	$\dot{x}_3 = -3k_3x_3$
$U_3 \xrightarrow{2k} U_2 + U_1$	$\dot{u}_3 = 3k_3x_3 - 2ku_3$
$U_2 \xrightarrow{k} 2U_1$	$\dot{u}_2 = \frac{4}{3}ku_3 - ku_2$

Solution are:

$$x_3 = \exp\,[-3k_3t]$$

$$u_3 = 3k_3A^{-1}\left\{\exp\,[-3k_3t] - \exp\,[-2kt]\right\}$$

$$u_2 = 4k_3(AB)^{-1}\left\{k\exp\,[-3k_3t] + B\exp\,[-2kt] - A\exp\,[-kt]\right\}$$

$$u_1 = 1 - x_3 - u_3 - u_2$$

$$t_m(u_3) = A^{-1}\ln\,(2k/3k_3)$$

$t_m(u_2)$ is given by:

$$3k_3 \exp\,[At_m] - A_{\exp}[kt_m] + 2B = 0$$

where

$$A = 2k - 3k_3 \text{ and } B = k - 3k_3$$

Cyclic tetramer III

Reactions:	Differential equations:
$X_4 \xrightarrow{4k_4} U_4$	$\dot{x}_4 = -4k_4x_4$
$U_4 \xrightarrow{2k} U_3 + U_1$	$\dot{u}_4 = 4k_4x_4 - 3ku_4$
$U_4 \xrightarrow{k} 2U_2$	$\dot{u}_3 = \frac{3}{2}ku_4 - 2ku_3$
$U_3 \xrightarrow{2k} U_2 + U_1$	$\dot{u}_2 = ku_4 + \frac{4}{3}ku_3 - ku_2$
$U_2 \xrightarrow{k} 2U_1$	

Solutions:

$$x_4 = \exp\,[-k_4t]$$

$$u_4 = 4k_4C^{-1}\left\{\exp\,[-4k_4t] - \exp\,[-3kt]\right\}$$

$$u_3 = 3k_4(CD)^{-1}\left\{k\exp\,[-4k_4t] + 2D\exp -[3kt] - C\exp\,[-2kt]\right\}$$

$$u_2 = 2k_4(CDE)^{-1}\{4k\,(k-k_4)\exp\,[-4k_4t] - DE\exp\,[-3kt] + \\ + 2CE\exp\,[-2kt] - 3CD\exp\,[-kt]\}$$

$$u_1 = 1 - x_4 - u_4 - u_3 - u_2$$

$$t_m(u_4) = C^{-1}\ln\,(3k/4k_4)$$

$t_m(u_3)$ is given by:

$$2k_4\exp\,[C\,t_m] - C\exp\,[kt] + 3D = 0$$

and $t_m(u_2)$ by:

$$3DE + 3CD\exp\,[2kt_m] - 16k_4(k-k_4)\exp\,[Ct_m] - 4CE\exp\,[kt] = 0$$

where

$$C = 3k - 4k_4,\ D = k - 2k_4 \text{ and } E = k - 4k_4.$$

4.3 *Methods of evaluation*

In the case of the cyclic dimer I, where the rate constants k_2 of the ring amide bond as well as that of the linear dimer (k) were both measured independently, complete verification of the theory was possible by comparing the chromatographically obtained data for u_2 as well as the results of the end group titrations with the former data.

As from end group titrations alone which merely give the sum of the end groups of ACA and its dimer (e.i. $u_1 + u_2/2$) the number of residues involved can not be derived. The latter was compared with the theoretical figure for $u_1 + u_2/2$ which approaches the value one for $t = \infty$ (cf. Fig. 2).

In the more complicated cases of the cyclic amides II and III, where only chromatographically obtained data on the approximate concentration of the linear intermediates were available, the equations for the times of maximum concentration t_m were applied, using again the value 0.36 h^{-1} for k.

Considering the experimentally estimated values of t_m as well as the maximum concentration of the relevant intermediate associated with that time, it was attempted by a number of trial and error calculations to evaluate the most probable value of the ring rate constant k_n which gave the best fit with the experimental data.

In the case of the cyclic diamide IV, where data on u_2 as well as on u_1 were determined while the rate constant k could be safely assumed to have the value 0.36 h^{-1} (see section 1), evaluation of k_2^* pertaining to the ring amide group could be evaluated from both u_2 and u_1.

5 *Results*

For the sake of brevity the results of the evaluation are only given in graphical representation in a sequence of plots of x_n and u_n against time for each cyclic amide X_n (Fig. 1 to 5). As previously set forth (section 4.1) x_n and u_n give the number of monomeric residues present in the determined quantity of the relevant hydrolysis product expressed as a fraction of that in the applied amount of starting material.

In the case of the Nylon 6.6 cyclic diamide (Fig. 5) the equal numbers of adipic acid and hexamethylene diamine residues are not distinguished and simply added together as representing u_1.

In all figures the points indicated are derived from experiments while curves represent the best theoretical fit corresponding with the rate constants as listed in Table 2 which represent the outcome of this investigation.

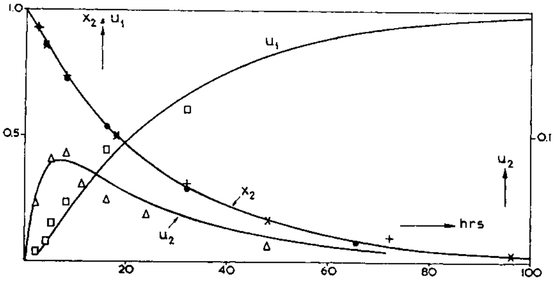

Fig. 1. Cyclic dimer (I). Experimental values for cyclic dimer (●, +, x); linear dimer (Δ) and monomer (□). Drawnout curves calculated for $k_2 = 0.019$ and $k = 0.36\ h^{-1}$. (Also see section 3.2)

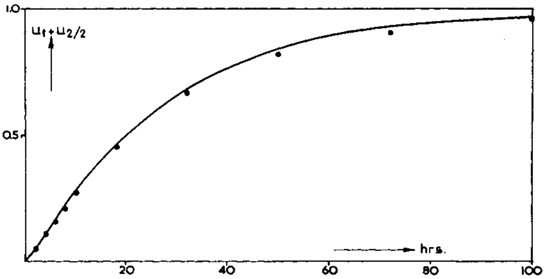

Fig. 2. Cyclic dimer (I). Values of $u_1 + u_2/2$ from end group titration (●), cf. section 4.3; curves calculated for $k_2 = 0.019$ and $k_2 = 0.36\ h^{-1}$

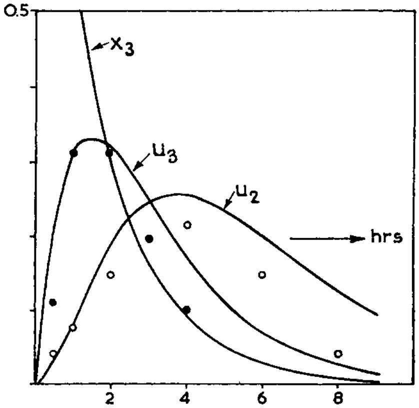

Fig. 3. Cyclic trimer (II). Experimental values for the intermediate linear products u_3 (●) and u_2 (○); curves calculated for $k_3 = 0.20$ and $k = 0.36\ h^{-1}$

(I) Cyclic dimer

The gravimetrically determined data for x_2 can be well represented by a curve exp $[-2k_2t]$ with $k_2 = 0.019\,hr^{-1}$ (Fig. 1).

The (less accurate) chromatographically estimated data for the linear dimer of ACA and for ACA (see 3.2.3) represented by triangles and squares (Fig. 1) fit reasonably well the theoretical curves corresponding with $k_2 = 0.019$ and $k = 0.36\,hr^{-1}$. As pointed out before, the value of the constant for the chain-amide bonds k was borrowed from earlier work[4]).

The sum of the amine and carboxyl end groups of ACA and its linear dimer determined by titration are converted into $u_1 + u_2/2$ (see 4.3). They also reasonably fit in the calculated curve (see fig. 2). The small systematic deviation, particularly noticeable at long reaction times, is an apparent one which can be traced back to a small systematic titration error. It has no bearing on the accuracy (± 0.002) with which the value of k_2 has been determined from the determination of x_2.

(II) Cyclic trimer

Evaluation of the experimental data for the cyclic trimer (as plotted in fig. 3) has led to $k_3 = 0.20\,h^{-1}$ as a reasonable approximation (compare curves calculated using this value).

Considering the fact that the cyclic trimer used is not completely pure (see 2), and the considerable experimental error in the chromatographic determinations, the accuracy is estimated to be $\pm\,0.05\,h^{-1}$. The very facts that $1.0 < t_m(u_3) < 2$ and $2.8 < t_m(u_2) < 4.5$ require already $0.15 < k_3 < 0.30$, thus indicating that the average rate constant for the amide bond in the cyclic trimer is anyhow somewhat smaller than that of the amide bond in a chain molecule.

(III) Cyclic tetramer

The experimental data found in the case of the cyclic tetramer together with curves calculated for $k_4 = 0.15$ are presented in Fig. 4. The observations of u_4 (linear tetramer; open squares) have been given less weight than those of u_3 and u_2. The estimated accuracy of k_4 is $0.05\,h^{-1}$.

(IV) Cyclic diamide of Nylon 6.6

In Fig. 5 the chromatographic determinations of u_2 (linear monoamide) are represented by open circles and those of u_1 (hexamethylene diamine) obtained from titration by triangles.

The observations of u_2 and u_1 appeared to be somewhat contradictory. The former, particularly at small reaction times, suggested $0.30 < k_2^* < 0.60$, whereas the latter give a better fit to curves corresponding to $0.55 < k_2^* < 0.80$.

It seems to be very unlikely that the rate constant k for the linear monoamide of Nylon 6.6 could differ significantly from 0.36 h^{-1}. It is felt that a solution of the discrepancy cannot be derived from the present material.

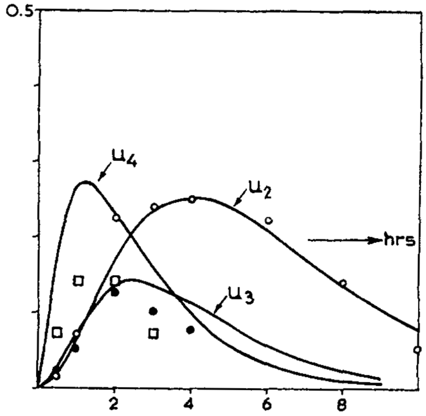

Fig. 4. Cyclic tetramer (III). Experimental values for the intermediate linear products u_4 (□) u_3 (●) and u_2 (○); curves calculated for $k_4 = 0.15$ and $k = 0.36\ h^{-1}$

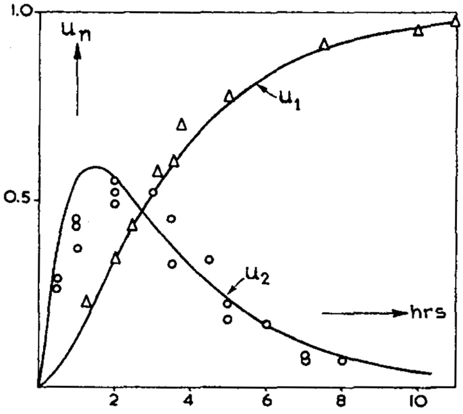

Fig. 5. Cyclic diamide (IV) from Nylon 6.6. Experimental values for the intermediate linear product u_2 (○) and the final product u_1 (△); cf section 3.5. Curves calculated for $k_2^* = 0.57$ and $k = 0.36\ h^{-1}$

Unfortunately, the constant k_2^* can therefore not be given with great accuracy and is believed to have its probable value between 0.50 and 0.60 h^{-1}.

Owing to the particular character of the mathematical functions in question, they appear to be rather insensitive to small changes in the assumed value of k_3^*.

6 *Discussion*

Apart from giving conclusive evidence on the correct molecular shape of the four cyclic oligoamides in question, the results reveal some remarkable differences in the sensitivity towards hydrolysis of the amide bond in the various molecules.

The hydrolysis rate constants (always pertaining to one CONH-group) vary over a wide range of about two orders of magnitude, (see Table 2, where the rate constants are collected along with the solubilities of the substances in water):

Table 2. Hydrolysis constants for amide groups in 7.72 N (25 per cent by weight) aqueous HCl at 110 °C. and solubilities in water in g. per 100 ml. at room temperature

Substance	Rate constant (h^{-1})	Solubility*) in water g./100 g.
linear polyamides	$k = 0.36 \pm 0.01$	–
cyclic dimer of caprolactam (I)	$k_2 = 0.019 \pm 0.002$	0.1
cyclic trimer of caprolactam (II). . . .	$k_3 = 0.20 \pm 0.05$	0.93
cyclic tetramer of caprolactam (III) . .	$k_4 = 0.15 \pm 0.05$	0.04
Nylon 6.6 cyclic diamide (IV)	$k_2^x = 0.55 \pm 0.10$	2.35
Caprolactam	$k \geqslant 2$*)	320

*) Borrowed from ref. 2.

i The amide bond in the 7-membered ring of caprolactam hydrolyses roughly ten times faster than that in linear molecules.

ii Of the two isomeric 14-membered cyclic diamides the one related to Nylon 6.6 (IV) hydrolyses about as fast as or somewhat faster than linear amides (cf. section 5) whereas the other isomer, the caprolactam dimer (I), shows remarkable resistance to hydrolysis with an approx. 15 times slower rate.

The investigations of HUISGEN⁷) and other authors have shown that in n-membered cyclic lactones and lactams there is a distinct difference in chemical properties between the lower members (n = 5 to 8) and the

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⁷) R. HUISGEN, Angew. Chem. **69** (1957) 341.

higher ones ($n \geqslant 10$). In the case of lactones, for instance, alkaline hydrolysis of the lower members proceeds several orders of magnitude faster than that of the higher ones.

The explanation of the difference is based on the fact that below the limit of $n=9-10$ the ester or amide group is, on steric grounds, compelled to assume the *cis*-form which has a higher energy than the *trans*-form. The latter occurs in the higher membered rings which are large enough to accomodate the *trans*-form without entailing undue strain. The *trans*-form is also preferred in linear molecules.

In the amides the *trans*-form is associated with a characteristic infrared absorption band at about 1550 cm^{-1} (6.45 μ), the "Amide II band". This band is absent in caprolactam and present in the linear oligo- and polyamides.

The fast rate of hydrolysis of caprolactam as compared to the linear and other cyclic amides thus seems to fit in with existing experience, in particular if one also takes into account that the 7-membered ring of caprolactam (in contrast to the 6 membered ring of δ-valerolactam) is somewhat strained, owing to crowding.

For the remarkable difference in behaviour between the two isomeric cyclic diamides we have, at the present moment, no (even tentative) explanation to offer. The models of both molecules can be built without any obvious strain with the amide groups either in the *cis*- or in the *trans*-form.

The infra-red absorption spectra of the two isomers as well as that of the cyclic trimer and tetramer all show the amide II-band at the same place and with about the same relative intensity. (The spectra of the four compounds are very similar and differ only in minor details).

The high resistance to hydrolysis of the caprolactam cyclic dimer along with its twentyfold smaller solubility in water as compared with its isomer (see Table 2) would suggest that in the molecule of the former, when in solution, the fields associated with the amide-groups are in some way screened off either by a steric effect or by some intramolecular interaction, not, or less, operative in the other isomer.

Upon examination of molecular models of the two isomers, the relative positions of the dipoles of the amide groups in the various possible conformations do not seem to give any obvious clue for an explanation. The one suggested by one of us in a preliminary paper²) cannot be upheld after further critical discussion.

We wish to acknowledge the contribution of our colleague, G. CHALLA, in this context.