ACIDOLYTIC CLEAVAGE IN THE POLYMERIZATION OF N-METHYLCAPRYLLACTAM INITIATED WITH ANHYDROUS HYDROGEN CHLORIDE*

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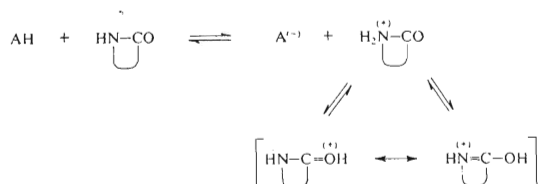
The deacylation cleavage of N-methylcaprylactam (1-methyl-1-aza-2-cyclononanone) and model N,N-dialkyl amides with hydrogen chloride was found to proceed at a considerable rate already at temperatures above 70°C. The formation of hydrochloride on N-methyl-ω-aminooctanoyl chloride is an initiation reaction and its condensation significantly contributes to the growth reaction in the cationic polymerization. At a temperature of 150–200°C acyl chloride group undergoes further reactions, which disturb the acidolytic equilibrium.

The cationic polymerization of lactams initiated with strong Brønsted acids (AH) gives rise to a protonized lactam, the N-protonized form of which exhibits high acylating activity:



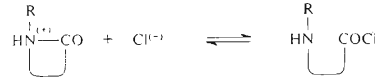
(*A*)

In a polymerization initiated with strong acids (such as HCl, HBr) the anion of the initiating acid always is a weaker nucleophile than the neutral lactam. Therefore, in lactams containing a hydrogen atom on the nitrogen atom, ring-opening acylation on the nitrogen atom is the predominant reaction:

(*B*)

* Part II in the series Polymerization of N-Substituted Lactams; Part I: This Journal *39*, 110 (1974).

The N-(ω-aminoacyl)lactam thus formed can then polymerize in the usual way[1,2]. In the case of N-substituted lactams, where reaction (*B*) cannot occur, the activated monomer can acylate only the anion of the initiating acid; initiation with hydrogen chloride gives rise to ω-aminoacyl chloride



(*C*)

which neutralizes another molecule of lactam hydrochloride or of free hydrogen chloride

(*D*)

The cleavage of the amide bond outlined above has been described for N,N-disubstituted benzamide, which at elevated temperatures reacts with hydrogen chloride with formation of benzoyl chloride and hydrochloride of the disubstituted amine[3].

The formation of salts of ω-aminoacyl halide could play an important role in the polymerization of N-substituted lactams, if reaction (*C*) proceeds at a rate comparable to that of the polymerization. It cannot be ruled out, however, that dealkylation cleavage described for dialkylamides[4] could also become operative in the polymerization of N-substituted lactams. Reaction (*C*) was therefore investigated in more detail, both with respect to its rate and equilibrium and to the composition of products.

EXPERIMENTAL

The melting points were determined on the heated stage of a microscope. Operations involving hydrochlorides of amides or of lactam were carried out in an inert atmosphere (nitrogen freed from oxygen, moisture content 3-4 p.p.m.).

Chemicals Used

N-*Methylcapryllactam* (1-methyl-1-aza-2-cyclononanone[5], *I*), rectified, was dried on a molecular sieve before the last distillation. Water content (after K. Fischer) was 0·0003%. Infrared spectrum (in substance): 1 397(m), 1 453(m), 1 475(m), 1 635(vs), 2 866(s), 2 933(vs), 3 020(w) cm^{-1}.

N,N-*Dihexylbutyramide* (II) obtained from dihexyl amine and butyric acid chloride with pyridine added in benzene solution[6] was rectified (151–153°C/4 Torr), dried with a molecular sieve and subjected to fractional distillation; according to GC and mass spectroscopy, the middle fraction used contained 0·08% of isomeric N,N-dialkylbutyramide and 0·02% of other impurities. Infrared spectrum (5% solution in CCl_4): 1 378(m), 1 465(m), 1 645(vs), 2 873(s), 2 932(vs), 2 960(s) cm^{-1}. For $C_{16}H_{33}NO$ (255·2) calculated: 5·49% N; found: 5·56% N.

N-*Butyrylpiperidine* (III) was prepared similarly to *II* from piperidine and butyric acid chloride, rectified, dried on a molecular sieve and redistilled (117—117·5°C/10 Torr); content of impurities after GC was 0·1%. Infrared spectrum (5% solution in CCl_4): 1 434(m), 1 466(m), 1 651(vs), 2 858(s), 2 940(vs), 2 964(s), 3 007(w) cm^{-1}. For $C_9H_{17}NO$ (155·2) calculated: 69·63% C, 11·04% H, 9·02% N; found: 69·38% C, 11·23% H, 8·91% N.

N-*Methylcaprylactam hydrochloride* (IV) has been described earlier[5]. Infrared spectrum (in a KBr disc): 1 326(m), 1 358(m), 1 422(s), 1 477(s), 1 608(s), 1 667(vs), 1 760(m), broad band 1 800—2 800 (maximum at 2 310, s), 2 870(s), 2 940(vs), 3 030(w) cm^{-1}.

N,N-*Dihexylbutyramide hydrochloride* (V) is a strongly viscous liquid. It was prepared by absorption of an equimolar amount of hydrogen chloride in amide at 0°C. Infrared spectrum in substance: 1 365 (m), 1 390 (m), 1 435 (s), 1 476 (s), 1 655 (vs), 1 755 (m), broad band 1 900 to 2 500 (maximum at 2 200, s), 2 862 (s), 2 936 (vs), 2 960 (s) cm^{-1}.

N-*Butyrylpiperidine hydrochloride* (VI) was prepared by introducing hydrogen chloride into an ether solution of *III* and dried at 25°C/2 Torr, m.p. 103—104°C (acetone) in a sealed capillary. Infrared spectrum (in a KBr disc): 1 390 (m), 1 434 (s), 1 468 (s), 1 670 (vs), 1 755 (m), broad band 1 900—2 800 (maximum at 2 230—2 320, vs), 2 860 (s), 2 955 (vs), 3 020 (w) cm^{-1}. For $C_9H_{17}NO.HCl$ (191·7) calculated: 5·22 mmol HCl/g; found by conductometric titration 5·23 mmol HCl/g.

Propanol was dried on a molecular sieve and rectified. Acetone was purified with potassium permanganate[7] and redistilled. The other compounds used were purified by repeated distillation and crystallization; benzoic acid was purified by sublimation.

Identification of the products of model reactions. From 4·6 g of the mixture *II* + *V* (2·99 mmol *V*/g) heated to 200°C for 3 h in a sealed ampoule, a solid compound (1·38 g) was filtered off after dilution with dry ether; the compound was identified as dihexylamine hydrochloride: m.p. 268 to 270°C (acetone, *cf.*[8]), weak acidity content 4·46 mmol/g (theor. 4·51 mmol/g), positive reaction with $NiCl_2 + CS_2$ and the molecular peak of dihexylamine (185, 2144) in the mass spectrum. Distillation of the liquid fraction under atmospheric pressure at a bath temperature 70—140°C yielded 1·21 g of a product with an intensive band at 1805 cm^{-1} belonging to acyl chloride. Reaction of the distillate with 0·8 g of aniline (refluxed 30 min in 100 ml of benzene) yielded 0·70 g of butyranilide. The fraction distilling at a bath temperature of 158°C (0·07 g) exhibited bands at 1 715 and 1 805 cm^{-1}. Further distillation of the reaction mixture *in vacuo* yielded 1·23 g of N,N-dihexylbutyramide contaminated by a compound absorbing at 1 725 cm^{-1}.

Acyl chlorides and amine hydrochlorides were detected both spectrophotometrically and alkalimetrically in mixtures arising by heating *IV* and *VI*. Aminolysis of the reaction mixtures in anhydrous piperidine (12 h/25°C) leads to the disappearance of bands in the regions of 1 800 and 1 720 cm^{-1}.

Quantitative Investigation of Acidolysis

Reaction procedure. Hydrochloride *IV* and *VI* was dissolved in lactam *I* or amide *III* respectively at 60°C with vigorous stirring during 10 min (in the case of amide *II*, HCl was introduced at 0°C) and the reaction mixture was transferred within 1—2 min into 10—25 thin-walled ampoules (per 50—400 mg). The HCl content was controlled titrimetrically, no volatilization of HCl could be observed, although the system was evacuated to 360 Torr during filling. The volume ratio of the gaseous and liquid phases was approximately 1 : 1. In some cases parallel experiments were carried out, with the volume ratio of the liquid and gaseous phases at the reaction temperature (100—200°C) being 10 : 1. Between the operations the samples were kept at −78°C. Experiments

in an open system were also carried out: an inert gas (10 ml/min) was passing through the mixture of *II* + *V*, and the volatile products were trapped in the freezer (−78°C) and in a 3% solution of barium hydroxide. The concentration of the unreacted monomer, M(mmol/kg), for calculations of the extent of the reaction, *p*, was determined by gas chromatography[5].

Method for determination of acyl chloride, amine hydrochloride and amide hydrochloride in acidolytic products. To determine acyl chloride in the presence of hydrogen chloride, the sample was titrated in anhydrous propanol

$$—COCl + C_3H_7OH \rightarrow —COOC_3H_7 + HCl \qquad (E)$$

and in aqueous acetone where moreover one equivalent of the carboxylic groups is also formed:

$$—COCl + H_2O \rightarrow —COOH + HCl \qquad (F)$$

Secondary amine hydrochloride, $R_2NH.HCl$, arising by the deacylating cleavage of amide along with an equimolar amount of acyl chloride according to reaction (*C*) and (*D*) is in no way affected by solvolysis. Conductometric titration allows to discern strong acidity (HCl, *i.e.* lactam or amide hydrochloride) from weak acidity (—COOH and $R_2NH.HCl$ are titrated together). Since the overall concentration of the acid components in the reaction mixtures equals the initial concentration of amide hydrochloride, the concentration of the weak acidity in the reaction mixture after alcoholysis, $[A_p]$, is equal to that of amine hydrochloride, $[A_p] = [R_2NH.HCl]$, and the concentration of the weak acidity, found after hydrolysis in aqueous acetone, $[A_a]$, is equal to the sum [—COOH] + $[R_2NH.HCl]$. Concentration of the acyl chloride groups is equal to that of the carboxylic groups in the hydrolyzed sample, [—COCl] = [—COOH], so that $[—COCl] = [A_a] - [A_p]$.

The yield of the deacylating cleavage according to reactions (*A*), (*C*), and (*D*) is defined as $q = ([R_2NH.HCl] + [—COCl])/[—CONR_2.HCl]_0 = 2[R_2NH.HCl]/[—CONR_2.HCl]_0$, where $[—CONR_2.HCl]_0$ is the initial concentration of lactam (or dialkylamide) hydrochloride.

Analyses. Ampoules with the reaction product were crushed under the surface of 15 ml of dry propanol or aqueous acetone (10% of H_2O), and the mixture was stirred in an inert atmosphere at 25°C (for model amides) or at 40—50°C (for polymers) for 30 min. In an aliquot portion (5—10 ml) completed with the same solvent up to 15 ml, the content of acids was determined by conductometric titration (0·1M sodium propoxide after alcoholysis, 0·1M aqueous NaOH after hydrolysis; consumption of reagents 0·3—0·4 ml). Blank tests for strong and weak acidity ($0·5—3.10^{-6}$ mol/15 cm^3) were determined for each medium from 6—10 titrations of mixtures of various amounts of standard compounds (*IV*, butyryl chloride, dibutyl amine hydrochloride, benzoic acid, in presence of *I*, *II*, and *III*) by linear extrapolation of the reagent volume to zero concentration of the standards.

The method and analytical procedure were verified on mixtures of butyryl chloride with *IV* and dibutyl amine hydrochloride in presence of *I*, *II*, or *III*; the average error of the determination of amine hydrochloride and acyl chloride was 2·5 and 3%, respectively.

RESULTS AND DISCUSSION

Main Reaction Products

Amine hydrochloride and acyl chloride were isolated and identified in the products arising on heating of N,N-dialkylamides (Figs 1,3 and Tables I—III). Their

formation can be described similarly to Eqs (*C*) and (*D*). Also the products of lactam *I* polymerization initiated with its hydrochloride *IV* were shown to contain acyl chloride and amine hydrochloride groups (Figs 1 and 2). These groups are present in an equimolar amount only for a certain time (Figs 2 and 3); later, especially at 150–200°C the concentration of acyl chloride decreases, and compounds absorbing at 1 720 cm^{-1} are formed (Fig. 1). Also gas chromatograms of alcoholyzed products from hydrochloride *V* contain – besides peaks of dialkylamine, propyl butyrate, and the initial amide *II* – other peaks pertaining to products of side reactions.

The decay of acyl chloride is most likely due to α-acylation of amide with formation of 3-oxoamide[9], as shown by absorption at 1 720 cm^{-1}. The consumption of acyl chloride shifts the equilibrium (*C*) to the right hand side. The corresponding increase in the yield of deacylating cleavage should be reflected in an increase in the concentration of amine hydrochloride. As a matter of fact, however, the concentration $R_2NH.HCl$ increases only insignificantly (Figs 2, 3), which suggests that also some

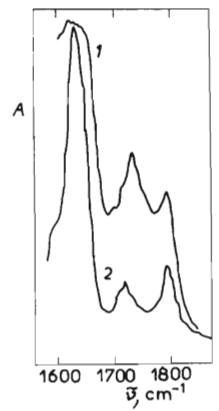


FIG. 1

Infrared Spectrum of the Products of Deacylating Cleavage at 150°C in the Wave Region 1 600–1 850 cm^{-1} (KBr cell flushed with dry nitrogen)

1 Thermolysate of N-methylcaprylactam hydrochloride (0·5 mol HCl/mol amide, after 3 h), *2* thermolysate of N-butyrylpiperidine hydrochloride (liquid fraction, after 3 h).

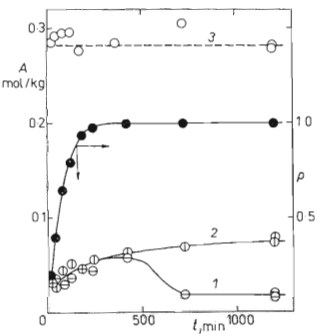


FIG. 2

Deacylating Cleavage During the Polymerization of N-Methylcaprylactam Initiated with 0·282 mol HCl/kg at 170°C

1 —COCl, *2* —NH,HCl groups, *3* total acidity of the polymerization product after alcoholysis with propanol; ● fraction of reacted monomer (*p*).

TABLE I

Thermolysis of Dialkylamides and N-Methylcaprillactam in Presence of Hydrogen Chloride (reaction time 3 h)

Amide	T °C	$[HCl]_0$ mol/kg	$[R_2NH.HCl]$ mol/kg	[—COCl] mol/kg	ν(C=O) cm^{-1}
I	200	5·22	2·25	0·02	1 732 (m)
I	150	2·78	0·56	0·42	1 795 (w), 1 732 (w)
II	200	2·99	—	—	1 805 (s), 1 715 (vw)
III	200	5·22	1·34	0·19	1 805 (s), 1 715 (vw)
III	150	2·69	0·70	0·46	1 798 (w), 1 720 (w)

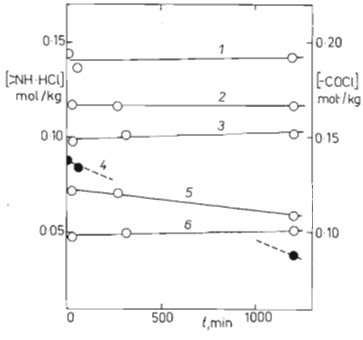


FIG. 3

Deacylating Cleavage of N-Butyrylpiperidine with Anhydrous Hydrogen Chloride

Content of piperidine hydrochloride (*1*—*3*) and —COCl groups (*4*—*6*) in the reaction product at an initial hydrogen chloride concentration of 0·635 mol/kg and a given temperature (°C); *1*, *4* 200; *2*, *5* 150; *3*, *6* 100.

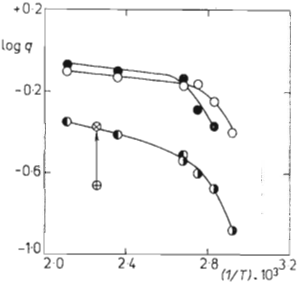


FIG. 4

Yield of Deacylating Cleavage, q, During the Acidolysis of Model N,N-Dialkylamides and Polymerization of N-Methyl Caprillactam

The data for q indicate, with some exceptions, extrapolated values to zero time from data in Table II and Fig. 3. Amide and the initial concentration of hydrogen chloride (mol/kg): N-butyrylpiperidine, 0·280 (◑), 0·635 (●); N,N-dihexylbutyramide, 0·463 (○), 1·821 (●); N-methylcaprillactam, 0·282, beginning of polymerization (p = 20%, ⊕), end of polymerization (p = 99·9%, ⊗).

other side reactions are operative. The dealkylating cleavage that may occur here[4] gives rise to olefins and monosubstituted amide. Their further transformations[1,2,10–12] extend the number of side products to include diacylamines, primary (or even tertiary) amines, and amidines.

Rate and Equilibrium of Deacylating Cleavage

Compared to the cleavage of N,N-diethylbenzamide[3], the deacylating cleavage of amides of aliphatic acids proceeds faster. Even short reaction times chosen for

TABLE II

Cleavage of Amide *II* with Hydrogen Chloride

$[A_t]$ denotes the total content of acidity (strong and weak) after alcoholysis. Meaning of the other concentration symbols is given in the Experimental; concentrations are in mol/kg.

T, °C	t, min	$[A_p]$	$[A_t]$	$[A_a]$	$[A_a] - [A_p]$
		$[HCl]_0 = 0{\cdot}463$ mol/kg			
70	300	0·073	0·457		
80	300	0·121	0·441		
90	300	0·159	0·465		
100	300	0·157	0·431	0·291	0·134
100	600	0·166	0·453		
100	1 440	0·160	0·465		
150	300	0·167	0·458		
150	1 440	0·172	0·475		
200[a]	300	0·235 (0·189)	0·510	0·344	0·109
200	600	0·178	0·467		
200	30	0·170	0·456		
		$[HCl]_0 = 1{\cdot}821$ mol/kg			
80	300	0·383	1·891		
100	300	0·677	1·775	1·231	0·554
100	1 440	0·669	1·789		
150	300	0·719	1·821		
200	300	0·775	1·840	1·487	0·704
200	1 440	0·792	1·839		

[a] In this experiment exceptionally $[A_t] > [HCl]_0$. Consequently, $[A_p]$ includes besides [≥NH.HCl] also another weak acidity. The value of [≥NH.HCl] calculated as the difference between $[HCl]_0$ and the content of strong acidity after alcoholysis is given in brackets.

the cleavage of the model amide *III* were too long as to allow kinetic measurements (Fig. 3). Formation of a considerable amount of amine hydrochloride and acyl chloride could be observed already when hydrochloride *VI* was dissolved in amide *III* during the preparation of the reaction mixtures.

The cleavage yield (q) in a closed system is higher than in an open one (Table III), when hydrogen chloride escapes from the reaction mixture. Only at 160°C the conversions in both systems are the same (Table III).

An evaluation of the equilibrium constants of the reactions (C) and (D) is made impossible because side reactions interfere with the equilibrium. A low effect of the initial concentration of amide hydrochloride on the yield of the deacylating cleavage was demonstrated for model amides. Fig. 4 shows that a fourfold increase in the concentration of $[HCl]_0$ in N,N-dihexylbutyramide did not affect the yield in the range under investigation. As may be expected from the character of reaction (C), the yield of the deacylating cleavage increases with temperature (Fig. 4).

Since there exists the disturbing effect of side reactions, and the dissociation equilibria and reaction kinetics could not be established yet, it has not been possible to formulate the mechanism of deacylating cleavage more precisely. Owing to the low dissociation constant of hydrogen chloride in dimethylformamide[13] ($K_a = 6{\cdot}5 \cdot 10^{-4}$ at 25°C) it is possible that even at elevated temperatures the concentration of protonized amide is low. It should be borne in mind at the same time that the acylating ability of N-protonized amide is exceptionally high, so that it may play an important role in the formation of acyl chloride and amine even at a low concen-

TABLE III

Thermolysis of Hydrochloride *V* in a Closed and Open System

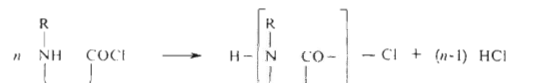
System	T °C	t min	$[HCl]_0/[II]$	R_2NH[a] %	Side products %[a]
Closed	200	15	0·275	10	0·3
Closed	200	60	0·275	10	0·5
Closed	200	330	0·275	12	1·5
Closed	160	60	0·275	8	0·5
Closed	240	60	0·275	11	0
Open[b]	160	180	0·241	8·5	0
Open	200	360	0·456	8	0·5
Open	230	180	0·679	5	0·5

[a] Concentration of dihexyl amine (or of the highest of peaks corresponding to the products of side reactions) determined by gas chromatography after alcoholysis of the sample with propanol (1 m column with silicone elastomer GEXE-60, 185°C); calculations based only on the peak area. [b] Determined in the nonvolatile fraction.

tration. The nonlinear dependence found in Fig. 4 may be explained by the fact that several reactions ((*A*), (*C*), (*D*)) participate in the cleavage, and also by the interference of side reactions.

Deacylating Cleavage of N-*Methylcapryllactam and Its Cationic Polymerization*

Unlike the cleavage of amides *II* and *III* (Figs 3 and 4, Table II), the cleavage of cyclic amide *I* (*C*) proceeds in a more complicated way (Fig. 2). In this case the concentration of acyl chloride does not attain the maximum at the beginning. Since ring closing of a nine-membered ring is very difficult, the cleavage of lactam *I* may be regarded as practically irreversible, which should lead to a 100% yield of acyl chloride and amine hydrochloride. However, the extent of cleavage at the beginning of polymerization is lower than for model amides, and later the maximum value of q approaches that obtained for the model amide *III* (Figs 3, 4). Obviously, reaction (*C*) cannot proceed to the end in this case, since it is immediately followed by fast polycondensation of the arising N-methyl-8-aminooctanoyl chloride:



(*G*)

Consequently, equilibria (*C*) and (*D*) could be attained only after completion of the polymerization, but the simultaneously occurring side reactions which consume acyl chloride cause its concentration to pass through a maximum (Fig. 2). Similarly to model amides, the thermodynamic constants of cleavage cannot be determined from these data.

While amine hydrochloride has only a low initiating activity in the polymerization of N-methylcapryllactam, the polymerization initiated with acyl chloride is very fast[5]. However, the polymerization initiated with lactam hydrochloride proceeds much faster than that with an equimolar amount of acyl chloride[5]. Moreover, the equilibrium concentration of acyl chloride is considerably lower than the initial concentration of lactam hydrochloride (Fig. 2). Consequently, the main growth reaction

(*H*)

cannot consist in transacylation H. The high polymerization rate observed for the

initiation with lactam hydrochloride may be explained by the fact that the main growth reaction is a bimolecular condensation of acyl chloride with amine in which

(J)

at least one of the reacting groups on the left side of the equation is part of the molecule of N-alkyl-8-aminooctanoyl chloride. This reaction disturbs the equilibrium (C); if lactam *I* is present, its cleavage leads to the formation of new acyl chloride and amine groups participating in the polymerization reaction (J). Hence, the majority of lactam is being incorporated into the polymer by the sequence of reactions (C) and (J), the concentration of the free amine being determined by equilibrium and

(K)

a corresponding equilibrium with the amide group in the polymer. A similar sequence of reactions with acyllactam as the reactive product instead of acyl chloride represents the main growth reaction in the cationic polymerization of unsubstituted lactams[2].

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