ALKALINE POLYMERIZATION OF 6-CAPROLACTAM. XLI.*
ANIONIC THERMOLYSIS OF N,2,2-SUBSTITUTED 3-OXOAMIDES

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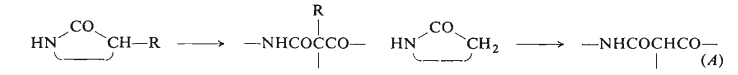
An uncatalyzed thermolysis of 2,2,4-trimethyl-N-ethyl-3-oxopentanamide gives rise to ethyl isocyanate and diisopropyl ketone only, while in the presence of the 5 mol% of sodium salt of 3-oxoamide a cyclic trimer of ethyl isocyanate, substituted barbituric acid, substituted 2,4,6-piperidinetrione and N-ethylisobutyramide are also formed. The latter compounds, along with ethyl isocyanate and diisopropyl ketone, represent about 90% of reacted 3-oxoamide. Their formation can be explained by isocyanate-ketone and ketene-amide cleavage, followed by reactions of isocyanate and ketene. In the ketene-amide cleavage of the oxoamide N-anion, the split-off ketene originates not in the ketonic, but in the amide acyl group; intramolecular cyclic rearrangement of the anion leads to diacyl amine.

Side reactions in the anionic polymerization of lactams yield thermally unstable derivatives of 3-oxoamides[1,2]. Lactams containing a methylene group in the vicinity of the carbonyl group produce α-monosubstituted 3-oxoamides, while α-monosubstituted lactams can give rise to α,α-disubstituted 3-oxoamides:



(A)

The reactions of α,α-disubstituted ketoamides are expected to be simpler then those of monosubstituted 3-oxoamides, and some products formed from α,α-disubstituted 3-oxoamides can be formed from α-monosubstituted 3-oxoamides as well. Thermolysis of α-monosubstituted 3-oxoamides yields ketone, amine and carbon dioxide, besides some compounds of uracil structure[2]; the latter compounds are produced as a consequence of N-carbamoylation of the initial 3-oxoamide by thermolytically formed isocyanate. According to Wiloth, the isocyanate is probably formed from 3-oxoamides as an intermediate[3] by thermolysis of corresponding ketimines. The formation of ketone is explained in terms of bimolecular non-hydrolytic cleavage[4]. In the case of α,α-disubstituted 3-oxoamides the isocyanate cleavage due to uncatalyzed thermolysis occurs without side reactions[5]. However, in the presence of a base, thermolysis has a more complex character; products have been isolated whose origin cannot be explained by isocyanate-ketone cleavage only, and it was suggested that ketene is formed as an intermediate[6]. The transformation of the 3-oxoamide structures is important both from the viewpoint of transformations

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of catalytic systems and foreign structures in anionic polymers and from that of their use as activators in the anionic polymerization of lactams[6,7].

In the present work, we have attempted to elucidate the reactions of α,α-disubstituted 3-oxoamides in an anhydrous medium in the presence of strong bases. The amount of 3-oxoamide structures represents only a fraction of the total amount of the polyamide, and an investigation of the behaviour of 3-oxoamides in the polymerization system is very difficult. Therefore these reactions were first studied on pure 3-oxoamides.

EXPERIMENTAL

The melting points were determined under a microscope with a heated stage (Boetius) and were not corrected. The infrared and ultraviolet spectra were recorded with spectrophotometers Perkin Elmer 457 and Cary 14, respectively, and the mass spectra were measured with an AEI 902 spectrometer. Perkin Elmer F-11 and F-21 instruments were used for the gas chromatographic measurements.

Chemicals

Lactone of 3-hydroxy-2,2,4-trimethylpentenoic acid, b.p. 120—122°C/150 Torr, was prepared according to ref.[8] from 2,2,4,4-tetramethyl-1,3-cyclobutanedione; amides of 2,2,4-trimethyl-3-oxopentanoic acid were obtained by addition of the above lactone to amines according to ref.[8]. 1,3-Diethyl-5,5-dimethylbarbituric acid was prepared from 5,5-dimethylbarbituric acid according to ref.[9]. 2-Isopropylidene-3-ethyl-5,5-dimethylperhydro-1,3-oxazine-4,6-dione was obtained similarly to ref.[10], m.p. 45—46°C (heptane). For $C_{11}H_{17}NO_3$ (211·1) calculated: 62·53% C, 8·11% H, 6·63% N; found: 62·72% C, 8·14% H, 6·80% N. 1-Ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione was obtained from the above oxazine by reaction with sodium methoxide[10], m.p. 35—36°C (heptane). Infrared spectrum (KBr, CCl_4): 1 685 and 1 715 cm^{-1}. Ultraviolet spectrum (methanol): λ_{max} 211 (log ε 4·03), 258 (log ε 2·19), and 267 nm (log ε 2·15). For $C_{11}H_{17}NO_3$ (211·1) calculated: 62·53% C, 8·11% H, 6·63% N; found: 62·60% C, 8·25% H, 6·58% N. 1,3,5-Triethyl-*s*-triazine-2,4,6-trione was obtained from ethyl iodide and sodium cyanate in dimethylsulfoxide according to ref.[11], m.p. 92—93°C (heptane). γ-Methylcaprolactam[12] was freshly redistilled before polymerization. N-Ethylhexanamide, b.p. 153—155°C/150 Torr, and N-ethylisobutyramide were prepared from acyl chlorides and ethyl amine[13,14]. N,N-Diethyltosylamide was obtained from *p*-toluene sulfochloride and diethyl amine, m.p. 61—62°C (heptane; 63°C in ref.[15]). Paraffin oil was treated as described in ref.[5].

Thermolysis in an Open System

Anionic thermolysis was carried out in an apparatus described earlier[5] under anhydrous conditions and in an inert atmosphere. To a known amount (about 2 g) of 3-oxoamide in paraffin oil, a measured volume of a 0·498M solution of triphenylmethyl sodium in tetrahydrofuran was added at 20—25°C, and the greatest part of solvent was removed during 5 min by short heating to 80°C under reduced pressure. After thermolysis, the distillate was dissolved in CCl_4 and the absorptions of isocyanate and ketone were measured in the regions 2 280 cm^{-1} and 1 715 cm^{-1}, respectively, similarly as in the uncatalyzed thermolysis[5].

Isolation and identification of products of the thermolysis of N-*ethyl*-2,2,4-*trimethyl*-3-*oxopentanamide*. Oxoamide (22·5 mmol), sodium hydride (1·73 mmol in the form of a 50% dispersion in mineral oil) were weighed into the reactor. To this mixture, 40 ml of anhydrous ether

were added; the oxoamide dissolved and reacted with sodium hydride. The ether was then distilled off, and the temperature was gradually increased (during 1 h to 75°C). As soon as the melt clarified, the reactor was immersed into a bath, 175°C, for 2 h. After this time, the residues of the distillate sticking to the condenser were transferred by heating into an absorber. Spectrometrically[5], 0·248 g of ethyl isocyanate and 1·778 g of diisopropyl ketone were determined in the distillate. To the rest (2·167 g), 50 ml of benzene and 1 ml of acetic acid were added, and the suspension thus obtained was extracted with 5 × 30 ml water. The aqueous layer was alkalinized with solid potassium hydroxide and extracted with ether; the residue (0·2 g) was obtained by evaporating ether. The aqueous layer was evaporated and the dry residue was extracted with ethanol. The organic acids were determined by gas chromatographic analysis[16] in the ethanolic extract after evaporation of ethanol. The solvent was removed from the benzene layer, and the liquid residue was fractionated by preparative gas chromatography (20% of silicone oil on Chromosorb at 120°C). The elementary composition of the individual fractions was determined by mass spectrometry. The composition of the individual chromatographic fractions was checked by comparing their infrared, and in some cases also mass spectra with the spectra of the authentic compounds.

Thermolysis of 1-(2,2,4-*trimethyl*-3-*oxopentanoyl*)*piperidine*. Amide (8·4 mmol) was thermolyzed at 220°C for 240 minutes in the presence of its sodium salt (0·35 mmol) Piperidine was identified in the distillate. The distillation residue contained about 90% of the initial oxoamide (estimated by gas chromatography). Two compounds were detected in the residue by means of mass spectrometry, the one having molecular weight 140·1078 and composition $C_9H_{17}NO$, identified as 1-isobutyrylpiperidide, and the other having molecular weight 210·1276, composition $C_{12}H_{18}O_3$; this compound could be the dimethyl ketene trimer.

Thermolysis of N-Ethyl-2,2,4-trimethyl-3-oxopentanamide in a Closed System

Sodium hydride (2·72 mmol in the form of a 50% oil dispersion) was dissolved at 55°C during 15 min in the melt of 54·6 mmol of oxoamide. This melt was filled into ampoules which after sealing were thermostated to 125°C. After chosen time intervals, the ampoules were cooled, the contents were transferred quantitatively into 5 ml of a cyclohexanone solution of anhydrous acetic acid (0·4 ml in 100 ml of cyclohexanone), and a weighed amount of naphthalene was added as the internal standard. The solution was chromatographed at 120°C on a capillary column (50 m) filled with Carbowax 20 M. The products and the unreacted amide were determined quantitatively after calibration with authentic compounds in concentrations approximately the same as in the real mixture.

The same reaction mixture was heated for 60 minutes at 174°C; the absorbancy of the methanolic solution of the product was 0·41 $g^{-1}\,l\,cm^{-1}$ at 270 nm.

Thermolysis of N-Ethyl-2,2,4-trimethyl-3-oxopentanamide in N-Ethyl-hexanamide

Sodium hydride (1·6 mmol) and 15·75 mmol of oxoamide were gradually dissolved in 59·3 mmol of N-ethyl-hexanamide, and the solution was then heated to 175°C for 60 minutes. Diisopropyl ketone formed in the reaction was trapped in the freezing trap. The residual ketone remaining in the solution was removed by heating to 50°C for 4 h at 20 Torr. The absorbancy of the unvolatile residue in methanolic solution was 1·08 $g^{-1}\,l\,cm^{-1}$.

Polymerization of γ-Methylcaprolactam in the Presence of 2,2,4-Trimethyl-3-oxopentanamide

The polymerization mixture prepared from 64·7 mmol of freshly distilled γ-methylcaprolactam, 1·86 mmol of sodium hydride and 16·38 mmol of oxoamide was heated to 175°C for 60 minutes.

The absorbancy of the methanolic solution at 270 nm was 0·575 g^{-1} l cm^{-1}. The polymerization mixture containing 79·5 mmol of γ-methylcaprolactam, 4·26 mmol of oxoamide and 4·39 mmol of sodium was treated in a similar manner. The absorbancy of the methanolic solution at 270 nm was 0·272 g^{-1} l cm^{-1}.

RESULTS AND DISCUSSION

From the products of base-catalyzed thermolysis of N,2,2,4-tetramethyl-3-oxopentanamide Baeder and Amann[6] isolated – besides diisopropyl ketone – also N-methylisobutyramide and 1,3,5,5-tetramethylbarbituric acid. From the products obtained by heating to 175°C N-ethyl-2,2,4-trimethyl-3-oxopentanamide in the presence of 7·36 mol% of its sodium salt, we isolated and identified 1-ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione together with diisopropyl ketone and the corresponding derivatives of isocyanate and barbituric acid. A compound having the composition $C_{13}H_{22}N_2O_2$ (238·34) was also detected, and supposed to be 1,3-diethyl-5,5-dimethyl-6-isopropylidene perhydro-1,3-diazin-2,4-dione. With the exception of isocyanate, the same products were also determined in the thermolysis of the ketoamide at a lower temperature in a closed system (Table I). On the whole, about 90% of the material were determined and identified. A residue of some 10% of undistillable substance remained in the reaction mixture. The products found in the experiments suggest that the decomposition of oxoamides in the presence of bases is a very complex process, and that similar conditions can also be expected in the anionic polymerization of α-substituted lactams.

TABLE I

Anionic Thermolysis of N-Ethyl-2,2,4-trimethyl-3-oxopentanamide at 125°C and 5 mol. % of its Sodium Salt in a Closed System

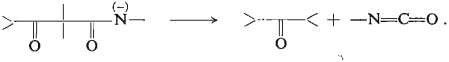
Found (mol/mol of initial amide): *a* initial amide, *b* diisopropyl ketone, *c* N-ethylbutyramide, *d* 1-ethyl-3,3,5,5-tetramethyl-2,4,6-trioxopiperidine, *e* 1,3-diethyl-5,5-dimethylbarbituric acid, *f* 1,3,5-trimethyl-*s*-triazine-2,4,6-trione. $Q_1 = b/c$, $Q_2 = c/(2d + e)$, $Q_3 = b/(d + 2e + 3f)$; *q* is the weight fraction of determined substances.

min	*a*	*b*	*c*	*d*	*e*	*f*	Q_1	Q_2	Q_3	*q*
60	0·215	0·60	0·30	0·028	0·17	0·033	2·0	1·3	1·2	0·87
120	0·110	0·58	0·29	0·023	0·19	0·035	2·0	1·2	1·1	0·87
180	0·094	0·59	0·28	0·025	0·18	—[a]	2·1	1·2	—	0·80
240	0·148	0·54	0·26	0·024	0·21	—[a]	2·1	1·0	—	0·77
300	0·080	0·65	0·27	0·025	0·21	—[a]	2·4	1·0	—	0·86
360	0·072	0·67	0·32	0·027	0·21	0·050	2·1	1·2	1·1	0·91
960	0·030	—[a]	0·27	0·023	0·19	0·056	—	1·2	—	—

[a] Undetermined.

Isocyanate-Ketonic Cleavage

Only isocyanate and ketone[5] (in ratio 1 : 1) are formed in the uncatalyzed thermolysis of α,α-disubstituted 3-oxoamides. On the contrary, when these 3-oxoamides are heated in the presence of their sodium salt, the amount of the ketone formed is less than the loss of 3-oxoamide (Table I). These observations indicate that oxoamide is also consumed in some other way than by isocyanate-ketone cleavage. Assuming that all the detected ketone was formed by isocyanate-ketone cleavage and did not react at the same time to yield other products, an equivalent amount of isocyanate should also be formed, according to



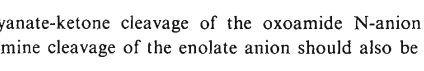
(*B*)

It follows from Table II, however, that throughout the reaction less isocyanate than ketone is formed. The difference is the greater the higher the boiling point of isocyanate; in the closed system, no free isocyanate could be found any more. One part of isocyanate disappeared by base catalyzed trimerization[17] (Table I). In a strongly basic medium, a part of isocyanate can be consumed according to Scheme 1.

However, an explanation of the formation of the products detected in the present study in terms of intramolecular acylation of carbamoylated oxoamides as intermediates is not quite satisfactory. The very small amount of uracil and fairly large quantities of the barbituric acid derivative indicate that the formation of the detected products must also be sought in other reactions than those indicated in Scheme 1.

Diketene-Amine Cleavage

Besides the isocyanate-ketone cleavage of the oxoamide N-anion the possibility of the diketene-amine cleavage of the enolate anion should also be borne in mind:



(*C*)

Such dissociation of oxoamides into amine and diketene has been considered by Mukaiyama and coworkers[18] for non-anionic (uncatalyzed) thermolysis of acetoacetamides. If both cleavage reactions (*B*) and (*C*) occurred simultaneously, the origin of the isolated compounds could be explained satisfactorily. (Scheme 2). Although piperidine and a compound resembling by its composition the dimethyl ketene trimer were

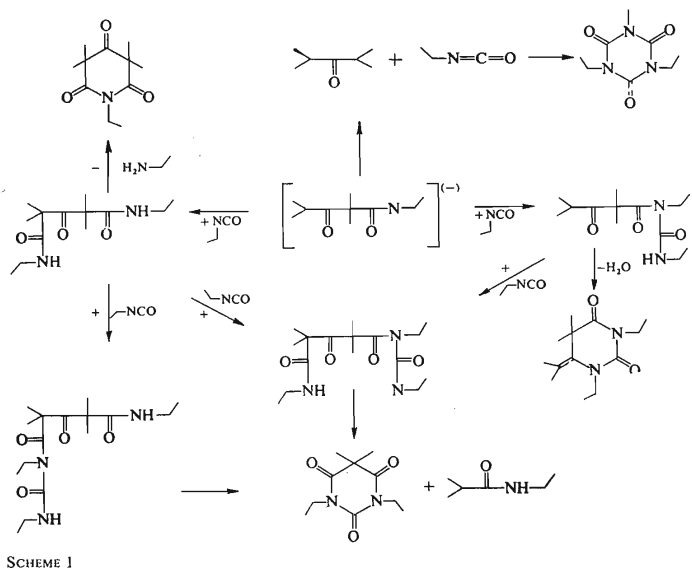
found in the presence of 1-isobutyrylpiperidine in the anionic thermolysis of 1-(2,2,4-trimethyl-3-oxopentanoyl)piperidine, the contribution of this type of diketene-amine cleavage to the formation of isolated products can be considered negligible, since no amine – neither free nor in the form of urea – was found in the products of thermolysis of N-ethyl-2,2,4-trimethyl-3-oxopentanamide.

Ketene-Amide Cleavage

Apart from undergoing cleavage into diketene and amine, the enolate or mesomeric oxoamide C,O-anion could also dissociate to yield ketene and amide:

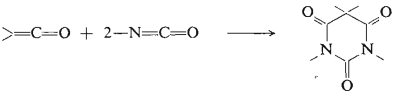
(D)

Such ketene-amide cleavage of the enolate anion is a formal analogue of the isocyanate-ketone cleavage of the oxoamide N-anion. Taking into account the simultaneous

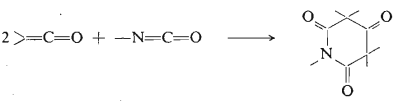


SCHEME 1

occurrence of the two types of cleavage of the oxoamide anions, it is easy to explain the formation of the isolated derivatives of barbituric acid and 3-oxoglutarimide from fragments from both types of cleavage, *i.e.*, ketene and isocyanate:

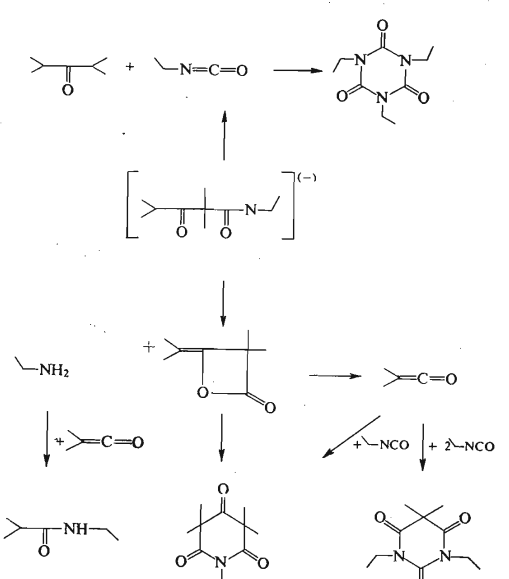


(*E*)



(*F*)

The formation of a derivative of barbituric acid and isocyanate has also been considered by Baeder and Amann[6]. Analogous additions of ketene to isocyanate yielding a 1 : 1 adduct are well known from the literature[19,20].

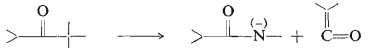


SCHEME 2

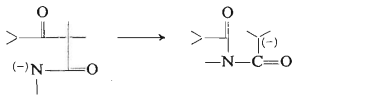
The formation of ketene during anionic thermolysis of oxoamides would also explain why, in the polymerization of caprolactam activated with N,2,2,4-tetramethyl-3-oxopentanamide, the isobutyryl group participated in the formation of the growth centres[6,21]. The forming ketene would acylate caprolactam while yielding N-isobutyrylcaprolactam as the growth centre. Acylation could of course take place also by a direct nucleophilic attack of the lactam anion at the ketonic carbonyl group. However, these two acylation reactions, be it by ketene or directly, are very improbable, since N,N,-disubstituted 3-oxoamides, from which no N-anion can be formed, do not participate significantly in the formation of growth centres[6,7]. Although no isocyanate can be formed from such oxoamide, both carbonyl groups are still accessible to the attack by the caprolactam anions, and also the formation of ketene ought not to be blocked thereby.

Ketene-Amide Cleavage or Rearrangement of the N-*anion*

It can be said, therefore, that in the formation of the growth centres only such a 3-oxoamide can take part – both by carbamoylation and by acylation – which can yield N-anions; oxoamide that cannot carbamoylate, but could acylate, does not participate in this reaction. This means that the participation of the acyl group can be explained only as an attack occurring at one of the carbonyl groups by the N-anion of the same molecule. This view is best met by intramolecular cyclic elimination (*G*) or rearrangement (*H*) of the N-anion



(*G*)



(*H*)

since the cyclic form of a molecule of the oxoamide N-anion is sterically favored, and the N-anion thus gets into the nearest proximity of the ketonic carbonyl group. It is very likely, therefore, that in the anionic thermolysis of N,2,2-trisubstituted 3-oxoamides, reactions (*G*) or (*H*), respectively, also take place, along with the isocyanate-ketonic cleavage. Simultaneous occurrence of both the above reactions can very well explain the origin of all identified products as well as the participation of the acyl group in the formation of growth-centres from oxoamides. This view is also corroborated by the quantitative representation of the individual products of the anionic thermolysis of N-ethyl-2,2,4-trimethyl-3-oxopentanamide in the closed system (Table I).

In the individual time intervals the molar ratio of diisopropyl ketone and N-ethylbutyramide formed in the reaction, Q_1, was equal to 2·1. As diisopropyl ketone is a product of the isocyanate-ketonic cleavage, and N-ethylisobutyramide is a product of the cyclic ketene-amide cleavage of the N-anion, the ratio thus obtained can be regarded as a ratio of the two types of cleavage.

The molar ratio of ketone to products derived from isocyanate, Q_3, is equal to 1·1; this value is close to that following from the suggested mechanism. If all ketene formed in reaction (*G*) were consumed in the formation of derivatives of barbituric acid and 3-oxoglutarimide then the molar ratio of amide and heterocycles, Q_2, should be equal to unity. A somewhat higher value of this ratio (Q_2 1·3) could mean that ketene has not reacted completely to yield the respective derivatives of barbituric acid and 3-oxoglutarimide. A part of ketene, or even isocyanate, could be consumed by polymerization or copolymerization[22], which might account for the origin of approx. 10% of the undistillable fraction.

The amounts of the products detected are in good agreement with the view that in the anionic thermolysis of N,2,2-trisubstituted 3-oxoamides the oxoamide N-anion or the sodium salt of oxoamide undergo intramolecular ketene-amide cleavage or rearrangement of the N-anion on the one hand, and isocyanate-cleavage on the other. The reactive fragments of this cleavage (ketene, or imide and isocyanate) then react with each other while yielding cyclic adducts (Table II).

Effect of N-*Alkyl Amides*

The anionic thermolysis of 3-oxoamides in a polymerization system is affected, on the one hand, by the fact that lactam as an amide can react with reactive fragments, and on the other, that as a polar solvent it increases the dissociation of the sodium salt, thus also raising the concentration of the oxoamide anions.

During the thermolysis of N-ethyl-2,2,4-trimethyl-3-oxopentanamide, products are formed which do not absorb in the region 270 nm. In the polymerization of lactam initiated with diacylamines or α-monosubstituted 3-oxoamides, however, products are obtained which strongly

TABLE II

Thermolysis of N-Ethylamide (5·078 mmol) and Anilide (2·677 mmol) of 2,2,4-Trimethyl-3-oxopentanoic Acid in the Presence of its Sodium Salts at 175°C in Paraffin Oil Solution in an Open System

Q is the ratio of isocyanate and ketone.

N-Ethylamide[a]				Anilide[b]			
Interval min	mmol		*Q*	Interval min	mmol		*Q*
	isocyanate[c]	ketone[d]			isocyanate[e]	ketone[d]	
0—30	0·40	0·73	0·5	0—14	0·28	1·13	0·25
30—90	0·45	0·48	0·94	10—20	0·18	0·70	0·25
90—135	0·39	0·46	0·85	20—30	0·10	0·31	0·31
135—180	0·39	0·46	0·84	30—45	0·08	0·16	0·48
				45—75	0·07	0·09	0·73

[a] Concentration 0·5046M (sodium salt $4{\cdot}948 \cdot 10^{-3}$M). [b] Concentration 0·2674M (sodium salt $4{\cdot}564 \cdot 10^{-3}$M). [c] Ethylisocyanate. [d] Diisopropyl ketone. [e] Phenylisocyanate.

absorb in the same region[1]. The absorbancy at 270 nm of the γ-methylcaprolactam polymerizate and that of the anionic thermolyzate of the N-ethyl-2,2,4-trimethyl-3-oxopentanamide in N-ethylhexanamide is higher than the absorbancy of the anionic thermolyzate of the 3-oxoamide alone (Table III).

This means that in the presence of an excess of N-alkylamide, and thus also in the polymerization mixture, there are also formed products (detectable by ultraviolet spectroscopy) other than in the case of the anionic thermolysis of N-ethyl-2,2,4-trimethyl-3-oxopentanamide in the melt. Therefore, the suggested mechanism of formation of products during the anionic thermolysis of N,2,2-trisubstituted-3-oxoamides holds only for the reaction in the melt. In the solution of an N-alkylamide which is not substituted in the vicinity of the carbonyl group, and thus also in the polymerization mixture containing caprolactam, the reaction will be affected particularly by the consecutive reactions of the reactive fragments. The formation of ultraviolet active substances starts probably with condensation reactions at the α-carbon atom of the

TABLE III

Absorbancy of Thermolyzates and Polymerizates

Amide or lactam	mmol			Absorbancy [b] $g^{-1}\,l\,cm^{-1}$
		Oxoamide[a]	NaH	
—	—	54·6	2·72	0·41
N-Ethylhexanamide	59·3	15·75	1·60	1·08
γ-Methylcaprolactam	64·7	16·38	1·86	0·575
γ-Methylcaprolactam	79·5	4·26	4·39	0·272

[a] N-Ethyl-2,2,4-trimethyl-3-oxopentanamide. [b] At 270 nm.

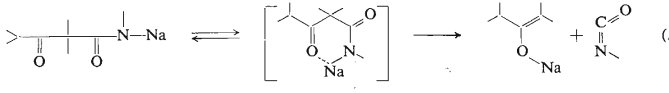
TABLE IV

Influence of Solvents on Anionic Thermolysis of 2,2,4-Trimethyl-3-oxopentananilide at 175°C in an Open System

c_a, c_s Initial concentrations of anilide and its sodium salt (mol/kg), respectively, c_k concentration of diisopropyl ketone after 30 min (determined by IR spectrophotometry).

Solvent	c_a mol/kg	c_s mol/kg	$c_k/c_a c_s$ kg/mol
Paraffin oil	0·371	0·0115	6·3
N,N-Diethyltosylamide	0·709	0·0275	1·8
N-Ethylhexanamide	0·741	0·0295	2·1

N-acylated and N-carbamoylated amide, respectively (lactam or its polymer). On the other hand, analogous N-acylated or N-carbamoylated derivatives of α-substituted amides undergo similar condensation reactions with more difficulty. The effect of the polarity of the solvent can be seen, *e.g.*, from Table IV. The anionic thermolysis of 2,2,4-trimethyl-3-oxopentananilide occurs in N,N-diethyl-*p*-tosylamide much slower than in paraffin oil. Since the above solvent supports the dissociation with the formation of the N-anion, there can occur, besides the cleavage of the 3-oxoamide anion, also the cleavage of the undissociated sodium salt *via* the transition state outlined below:



(*I*)

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