CATALYTIC ACTIVITY OF THE TRANSFORMATION PRODUCTS OF 3-OXOAMIDES IN THE ANIONIC POLYMERIZATION OF CAPROLACTAM*

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The catalytic activity of some heterocyclic compounds formed from 3-oxoamides under the conditions of the anionic lactam polymerization was investigated. While no activation effect was observed for 1,3,5,6-tetrasubstituted pyrimidine-2,4-dione, the derivatives of 1,3,5-trisubstituted *s*-triazine-2,4,6-triones and of tetrasubstituted pyrimidine and pentasubstituted piperidine-2,4,6-triones exhibit an important catalytic activity comparable with that of acyllactams. Consequently, some decay products of 3-oxoamide structures may considerably contribute to the regeneration of the catalytic activity.

During the anionic polymerization of caprolactam or α-alkylcaprolactam the diacylamine structures of the growth centres are transformed by condensation and transacylation reactions into 3-oxoamide structures which are effective activators of the anionic polymerization of lactams[1,2]. Under the polymerization conditions, *i.e.* in the presence of a strong base, amides of 3-oxo acids are transformed into a number of compounds[1-4] some of which should exhibit catalytic activity similarly to 3-oxoamides or diacylamines. Moreover, these products may contribute to changes in the basicity of the system. Since the decay and regeneration of the activity of the catalytic system are of a great importance, we investigated the effect of some decay products of N,2-disubstituted and N,2,2-trisubstituted 3-oxoamides which are model compounds of the 3-oxoamide structures contained in the anionic polymers of caprolactam and of α-substituted caprolactam.

EXPERIMENTAL

1,3-*Dimethyl*-5,5-*disubstituted barbituric acids* (Table I) were obtained by the methylation of 5,5-disubstituted barbituric acids with dimethyl sulfate similarly to a procedure described earlier[5]. The other tetrasubstituted barbituric acids (Table I) were prepared from the respective phenyl urea by a reaction with 2,2-dimethylmalonic acid dichloride in 1,2-dichloroethane[8].

* Part LV in the series Alkaline Polymerization of 6-Caprolactam; Part LIV: This Journal *39*, 2212 (1973).

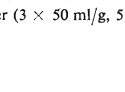
1,3-*Diphenyl*-5,5-*dimethyl*-2-*thiobarbituric acid* was obtained from 2,2-dimethylmalonyl chloride and N,N'-diphenylthiourea, m.p. 201–202°C (cyclohexane). For $C_{18}H_{16}N_2O_2S$ (324·4) calculated: 66·8% C, 4·98% H, 8·63% N; found: 66·9% C, 5·06% H, 8·38% N.

1-Ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione was obtained according to ref.[9] (cf. ref.[3]). 1,3,5-Triethyl-s-triazine-2,4,6-trione was prepared from ethyl iodide and sodium cyanate in dimethyl sulfoxide similarly to ref.[10], the other triazines used were obtained by trimerization of isocyanates according to ref.[11]. 1,3-Diphenyldiaza-2,4-cyclobutanedione was prepared according to ref.[12]. Polyphenylisocyanate was obtained by the polymerization of phenyl isocyanate with sodium cyanide in dimethylformamide according to ref.[13].

Polymerization. Sodium caprolactam[14] and the tested compound were dissolved stepwise in caprolactam at 100°C. The ampoules were filled in a filling device described earlier[15] and heated under conditions given in Tables II and III. For the determination of the yield (*p*) the polymerizate was crushed, extracted with boiling water (3 × 50 ml/g, 5 min each time), and dried to constant

TABLE I

Tetrasubstituted Barbituric Acids



R^1	R^2	R^3	R^4	M.p., °C	Composition (m.w.)	Calculated/Found		
						% C	% H	% N
C_2H_5	C_2H_5	CH_3	CH_3	36–38[a]	$C_{10}H_{16}N_2O_3$	56·60	7·60	13·20
					(212·1)	56·60	7·70	12·95
CH_3	CH_3	C_6H_5	H	156–156·5	$C_{12}H_{12}N_2O_3$	62·06	5·21	12·07
					(232·2)	62·24	5·41	12·08
	CH_3	CH_3	C_6H_5 C_6H_5	233–234[b]	$C_{18}H_{16}N_2O_3$	70·12	5·23	9·09
					(308·3)	70·20	5·36	9·18
CH_3	CH_3	C_6H_5	CH_3– 	179–180·5	$C_{19}H_{18}N_2O_3$	70·79	5·63	8·69
					(322·4)	71·05	5·69	8·67
CH_3	CH_3	C_6H_5		148–149	$C_{19}H_{18}N_2O_3$	70·79	5·63	8·69
					(322·4)	70·90	5·86	8·80
CH_3	CH_3	C_6H_5	CH_3O– 	169–170	$C_{19}H_{18}N_2O_4$	67·47	5·33	8·28
					(338·3)	67·31	5·46	8·60
CH_3	C_6H_5	CH_3	CH_3	90–90·5[c]	$C_{13}H_{14}N_2O_3$	63·40	5·75	11·37
					(246·3)	63·20	5·90	11·67

[a] According to ref.[5]. [b] M.p. 230–232°C according to ref.[6]. [c] M.p. 88–89°C according to ref.[7].

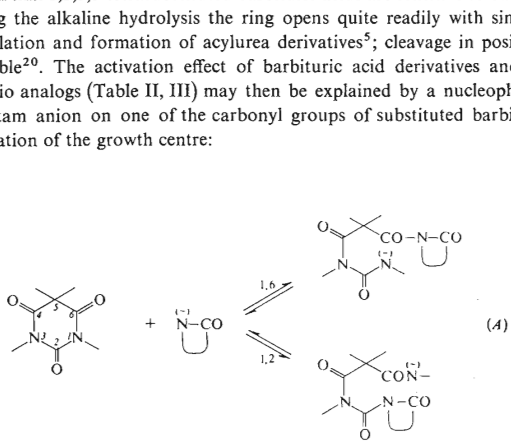
weight. The intrinsic viscosity of the polymer was calculated from the viscosity of a cresol solution at $c = 0{\cdot}4$ g/dl and $k_H = 0{\cdot}4$.

RESULTS AND DISCUSSION

Of the products arising by the anionic thermolysis of model 3-oxoamides[3,4] only those were investigated for which one can expect rather important effects and which are formed in a major amount. It is known that aliphatic N-alkylamides do not influence the polymerization almost at all[16]; we therefore did not investigate the activation effect of N-alkylbutyramide and N,N′-2--trialkylmalonamide representing some of the structures arising from the 3-oxoamide structures under polymerization conditions[4]. For the same reasons, ketones were not studied in more detail, because their effect will be rather retardative owing to the possibility of their base catalyzed condensation; the inhibitive effect of ketone was described *e.g.* for the anionic polymerization of laurolactam[17]. The effect of carbon dioxide or of sodium carbonate[18] and urea derivatives[19] has been investigated earlier. 1,3,5-Triethyl-6-propylpyrimidine-2,4-dione formed by the anionic thermolysis of N,2-diethyl-3-oxohexanamide[4] behaved quite inertly already during the preliminary polymerizations. Therefore, only those compounds were investigated in greater detail the structures of which are formed by the anionic thermolysis of N,2,2-trialkyl-3-oxoamides[2,3], *i.e.* derivatives of *s*-triazine (*I*), barbituric acid (*II*), and piperidinetrione (*III*) (Scheme 1). These compounds are probably formed during the anionic polymerization by reactions of isocyanates, which are precursors of the growth centres. Compounds *I*—*III* may be in equilibrium with the initial compounds under the polymerization conditions, thus producing the growth centres.

Substituted Barbituric Acids and 2,4,6-*Piperidinetrione*

It is known that 1,3,5,5-tetrasubstituted barbituric acids are sensitive to bases, so that *e.g.* during the alkaline hydrolysis the ring opens quite readily with simultaneous decarboxylation and formation of acylurea derivatives[5]; cleavage in position 1,2 is also possible[20]. The activation effect of barbituric acid derivatives and of some of its 2-thio analogs (Table II, III) may then be explained by a nucleophilic attack of the lactam anion on one of the carbonyl groups of substituted barbituric acids with formation of the growth centre:



(*A*)

TABLE II

Anionic Polymerization of Caprolactam in the Presence of 0·4 mol.% of Sodium Caprolactam (c_1) and 0·134 mol.% of Activator (c_A)
t Polymerization time in min, p yield of polymer in %, $[\eta]$ intrinsic viscosity in dl/g.

Activator	120°C			175°C		220°C		
	t	p	$[\eta]$	t	p	t	p	$[\eta]$
1,3,5-Triethyl-*s*-triazine-2,4,6-trione	90	1·08	—	10	10·9	10	85·8	3·84
	240	7·58	1·14	—	—	60	91·9	2·75
1,3,5-Triphenyl-*s*-triazine-2,4,6-trione	30	37·0	1·04	10	91·9	10	91·7	2·46
	—	—	—	—	—	60	91·3	2·41
1,3,5-Tridodecyl-*s*-triazine-2,4,6-trione	120	4·6	—	—	—	10	91·0	—
1,3-Diphenyldiaza-2,4-cyclobutanedione	120	66·5	—	10	92·1	10	91·2	—
Poly(N-phenylcarboxamide)	120	1·1	—	10	93·0	10	89·1	—
	—	—	—	—	—	60	91·4	—
1-Ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione	50	2·1	—	10	46·9	10	91·9	1·84
	120	5·0	0·88	—	—	60	92·0	1·90
2-Isopropylidene-3-ethyl-5,5-dimethylperhydro-1,3-oxazine-4,6-dione	55	1·5	—	10	29·1	60	92·0	2·47
	120	5·0	0·94	—	—	60	91·6	2·37
1,3-Dimethyl-5,5-diethylbarbituric acid	20	1·1	—	10	10·7	10	89·4	4·28
	120	2·1	—	—	—	60	92·3	3·00
1-Phenyl-5,5-dimethylbarbituric acid	30	1·4	—	—	—	10	76·5	1·89
	48	3·1	—	—	—	60	85·5	1·89
1,3,5-Trimethyl-5-phenylbarbituric acid	120	5·3	—	—	—	120	86·9	1·87
	—	—	—	10	34·0	—	—	—
1,3-Diphenyl-5,5-dimethyl-4-thiobarbituric acid	30	2·0	—	10	90·6	10	91·6	2·53
	45	2·4	—	—	—	60	91·5	2·43
1-Phenyl-3-(3′-tolyl)-5,5-dimethylbarbituric acid	23	3·03	0·39	—	—	10	91·8	1·99
	30	6·3	0·59	10	67·6	60	91·1	1·90
	120	15·9	1·03	—	—	120	92·0	1·86
1,3-Diphenyl-5,5-dimethylbarbituric acid	15	6·5	—	—	—	—	—	—
	30	13·0	—	—	—	—	—	—
	60	24·0	—	—	—	—	—	—

1-Phenyl-3-(4′-tolyl)-5,5-dimethylbarbituric acid	18	4·3	—	—	—	10	89·4	1·98
	30	5·7	0·57	10	76·6	60	91·7	1·80
	120	28·7	1·35	—	—	120	91·8	1·77
1-Phenyl-3-(4′-methoxyphenyl)-5,5-dimethylbarbituric acid	12	6·4	—	—	—	10	91·6	2·47
	30	14·4	0·99	10	82·0	70	91·7	2·33
	120	40·0	1·55	—	—	120	91·5	2·28
N-Benzoylcaprolactam	—	—	—	10	79·8	—	—	—
2,2,4-Trimethyl-3-oxopentane-*p*-methylanilide	—	—	—	10	92·5	—	—	—

TABLE III

Effect of the Activator Type on Molecular Weight of the Anionic Polymer
Meaning of the symbols *cf.* Table II.

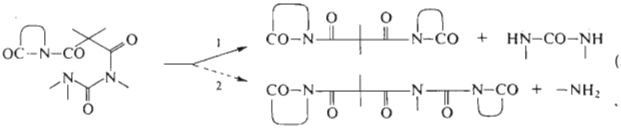
Activator	C_I	C_A	°C	Course, min			p	$[\eta]$
				no flow	turbidity	total		
1,3,5-Triethyl-*s*-triazine-2,4,6-trione	0·5	0·5	175	14	35	60	95·6	4·73
1,3,5-Triphenyl-*s*-triazine-2,4,6-trione	0·5	0·5	175	4	5	30	96·3	3·90
1,3,5-Tridodecyl-*s*-triazine-2,4,6-trione	1·05	6·25	175	4	3	60	90·0	2·50
Poly(N-phenylcarboxamide)	0·5	0·4	175	1	3	30	97·7	2·39
1-Ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione	0·3	0·25	173	5	10	30	97·0	5·77
1-Ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione	0·3	0·3	150	16	23	60	97·5	6·96
1-Ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione	0·3	0·9	210	—	—	30	90·6	2·14
1-Ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione	0·3	0·2	175	—	—	30	10·0	—
1,3-Dimethyl-5,5-diethylbarbituric acid	0·3	0·3	175	9	—	25	43·0	6·54
1,3-Dimethyl-5,5-diethylbarbituric acid	0·3	0·93	210	2	—	30	90·5	4·82
1,3-Dimethyl-5,5-diethylbarbituric acid	0·3	0·2	175	—	—	30	10·0	—

The nucleophilic attack at the carbonyl groups is affected by the polar effects of the adjacent groups. In a polymerization activated by tetrasubstituted derivatives of barbituric acids with various substituents on one of the adjacent nitrogen atoms the catalytic activity increases in the following order of substituents (Table II):

$$m\text{-tolyl} < \text{phenyl} < p\text{-tolyl} < p\text{-methoxyphenyl} .$$

The effect of substitution in position 5 is similar. As can be seen from Table II, the activation effect of 1,3,5-trimethyl-5-phenylbarbiturate is much stronger than for 1,3-dimethyl-5,5'-diethylbarbiturate. The catalytic activity considerably diminishes if hydrogen is one of the substituents at the nitrogen atom; the derivative having hydrogen atoms on both nitrogen atoms does not exhibit catalytic activity any more, because these compounds are strong acids[21].

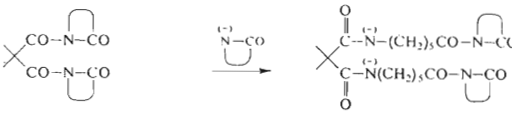
Molecular weights or intrinsic viscosities of polymers obtained at lower temperatures are much higher (Tables II, III) than with activators of the acyllactam type; at higher temperatures the difference becomes much smaller. One of the causes of the high molecular weight attained with the compounds under investigation at lower temperatures could consist in the low extent of formation of the growth centres, the activation energy of the initiation reaction (*A*) being high. The high molecular weight could also be due to the formation of species with two growth centres, similar to those arising from diisocyanates or bis-3-oxoamides:



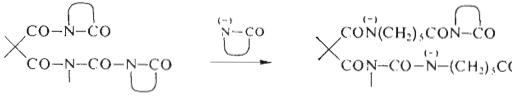
Such compounds yield much higher molecular weights[1,19] than acyllactam activators of the acyllactam type. This may be also due to the decrease of the basicity of the system, which suppresses degradation. The effect of the decrease of the basicity of the catalytic system is particularly obvious if a more acidic activator is used; *e.g.* with 5,5-dimethyl-3-phenylbarbituric acid the molecular weight at 220°C and 240°C is more stable than with activators which do not contain an acidic hydrogen (Fig. 1). The higher stability of molecular weights obtained with derivatives of barbituric acids with aromatic substituents on both nitrogen atoms (compared to similar activators with aliphatic substituents) may also be explained by the difference in the acidities of the end groups of macromolecules.

The primary growth centres, the formation of which is shown in reactions

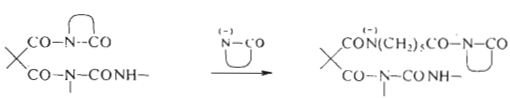
(*A*) and (*B*), can yield, by further addition of lactam anions, a different growth centre (*C*–*E*):



(*C*)

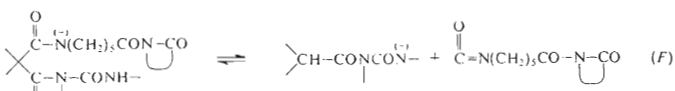


(*D*)



(*E*)

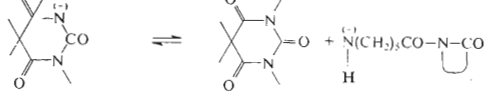
These structures, and particularly the compounds obtained by reactions (*D*) and (*E*), could undergo isocyanate cleavage with simultaneous release of a strong base, similarly to the cleavage of the 3-oxoamide N-anions[1,3]:



(*F*)

(*IV*)

The cleavage of the tautomeric form of anion *IV* regenerates the initial barbiturate,



(*G*)

while the growth centre of the aminocaproylcaprolactam type remains preserved.

Generally the reactions considered above proceed during the polymerization to different extents. It seems that especially the reactions (*E*) and (*F*) will play an important role in the activation mechanism. Both these reactions best explain the formation of high-molecular weight polyamide, the fast decrease in the basicity of the system, and the comparatively slow decrease in the molecular weight.

Also 1-ethyl-3,3,5,5-tetramethyl-2,4,6-piperidinetrione, the structure of which corresponds to one of the decay products of N,2,2-trisubstituted 3-oxoamides[3], exhibits a high activation effect (Tables II and III). Obviously, there is a nucleophilic attack on the carbonyl groups with the opening of the heterocycle during the polymerization, similarly to the derivatives of barbituric acid. The formation of a high-molecular weight polymer may be explained similarly to the activators of the barbiturate type.

Cyclic and Linear Oligomers of Isocyanates

During the activation of the anionic polymerization with 3-oxoamides the primary carriers of their catalytic activity are isocyanates[1] which can cyclotrimerize during

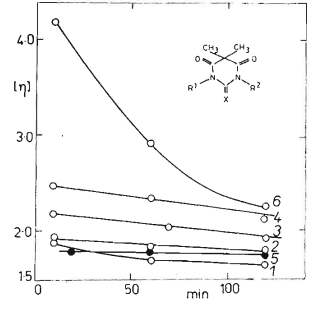


FIG. 1

Change in Intrinsic Viscosity During the Polymerization of Caprolactam at 220°C Catalyzed with 0·4 mol.% of Sodium Caprolactam and 0·13 mol.% of Activator

Curve (R^1, R^2, X): *1* (*p*-methylphenyl, phenyl, 0); *2* (*m*-methylphenyl, phenyl, 0); *3* (*p*-methoxyphenyl, phenyl, 0); *4* (phenyl, phenyl, S); *5* (phenyl, H, 0); *6* (methyl, methyl, 0); holds for 5,5-diethyl derivative).

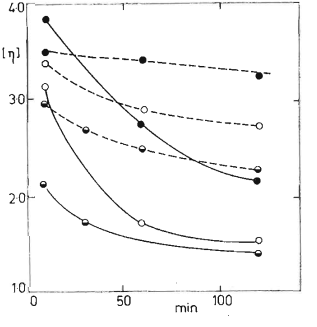
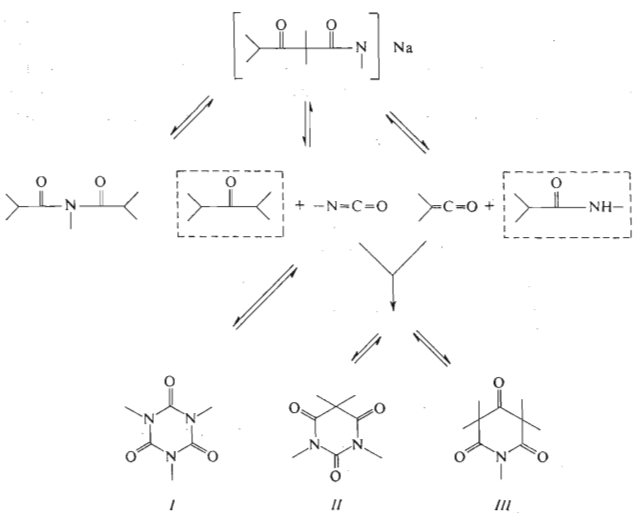


FIG. 2

Change in Viscosity During the Polymerization of Caprolactam at 220°C (●), 240°C (○), and 270°C (◒) in the Presence of 0·4 mol.% of Sodium Caprolactam and 0·134 mol.% of 1,3,5-Triphenyl (– – –) or 1,3,5-Triethyl-*s*-triazine-2,4,6-trione (———)

the anionic polymerization, thus contributing to the branching or crosslinking of the polymer. Although the cyclic trimers of isocyanates are thermally very stable[22], their carbonyl groups readily undergo nucleophilic attack, similarly to alkaline hydrolysis[23] or hydrazinolysis[24]. Their high activation effect is therefore by no means surprising (Tables II, III). As expected, the catalytic effect is also influenced by substitution on the nitrogen atom, and is much higher for aromatic substituents than for the aliphatic ones. The activation effect is not restricted only to the cyclic trimers or dimers[25] of isocyanates. The growth centres are also formed from their linear polymers[26] (Table II). The higher thermal stability of molecular weights of polymers prepared in the presence of triaryl-*s*-triazine-2,4,6-triones compared to polymers obtained by activation with trialkyl derivatives (Fig. 2) can be explained by the different acidity and cleavage of the respective N-alkyl and N-arylurea structures.

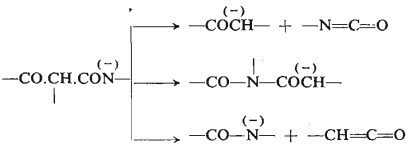
For N-2-disubstituted 3-oxoamide structures, which are part of the polyamide chain, the regenerated activator component only consists of isocyanate, or of ketene



SCHEME 1

Compounds Arising from N,2,2-Trisubstituted 3-Oxoamides under Conditions of Anionic Polymerization (framed compounds inactive)

or diacylamine arising by cleavage of the 3-oxoamide N-anion[4]



Although the trimer of isocyanate forms readily in a basic medium, it is most likely not formed under the conditions of the anionic polymerization of lactams, because isocyanate is consumed, besides the formation of the growth centres, also by side reactions with formation of the derivatives of malondiamide and pyrimidinedione[4]. The transient C-acyl derivative of malonamide is readily deacylated to yield acyllactam growth centres; at the same time however, and equivalent of 3-oxoamide is consumed, which also is capable of forming the growth centres.

Since the activity of compounds *I–III* (Scheme 1) is comparable with that of the acyllactam type compounds, tetrasubstituted barbituric acids contribute – along with the respective derivatives of persubstituted 3-oxoglutarimides and with isocyanurates – to the regeneration of the catalytic activity during the anionic polymerization of lactams with N,2,2-trisubstituted 3-oxoamides as activators, or during the anionic polymerization of α-substituted lactams.

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