

KINETICS OF THE INITIAL STAGE OF INITIATED THERMAL OXIDATION OF CAPROLACTAM AND N-OCTYLBUTYRAMIDE

Božena LÁNSKÁ^a, Ludvig Michailovich POSTNIKOV^b,
Albert Leonidovich ALEKSANDROV^b and Jan ŠEBENDA^a

^a *Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6 and*

^b *Institute of Chemical Physics,
Academy of Sciences of the USSR, Moscow, USSR*

Received March 16th, 1981

The thermal oxidation of ϵ -caprolactam or N-octylbutyramide in the liquid phase is a chain radical reaction. In the initial stage, the only reaction product is the corresponding amide hydroperoxide, formed from peroxy radicals by a second-order termination reaction. The rates of thermal oxidation reactions initiated with 7,7'-dicumenyl peroxide or 1,1'-azodi(cyclohexanecarbonitrile) and the rates of initiation reactions were measured in the temperature range 80–130°C. Using the values thus obtained, the ratios of rates of the propagation and termination steps, $k_2 \cdot k_6^{-1/2}$, characterizing the oxidizability of compounds, were calculated.

6-Hexanelactam (ϵ -caprolactam), 12-dodecanelactam (lauro lactam) and prospectively 8-octanelactam (caprylolactam) are monomers important for the synthesis of polyamides. The course of the polymerization of lactams and the properties of polymers depend considerably on the quality of the initial monomer. Hydrolytic polymers of caprolactam prepared from the latter with a rather low content of caprolactam hydroperoxide have a lower molecular mass and a higher content of carboxylic groups as compared with polymers prepared from caprolactam free from hydroperoxide¹. At the same time, polyamides with a higher content of carboxylic groups exhibit a distinctly lower thermooxidative stability than polymers with an equimolar content of amino and carboxy groups². Since caprolactam hydroperoxide is the primary product of the oxidation of caprolactam^{1,3} and since, moreover, lactams may undergo oxidation during their preparation, storage, transport and melting before the polymerization process, attempts were made to characterize the oxidizability of the individual lactams.

The existing knowledge of the oxidation of linear N-alkylamides^{4–6} allows us to conclude that the autooxidation of these amides is a chain reaction having an autocatalytic character and that the kinetic data are not completely analogous to those observed in the oxidation of hydrocarbons. The views expressed about the kinetics of autooxidation of caprolactam are not uniform^{1,3}; it has been proved,

however, that caprolactam hydroperoxide, which reacts further to give rise to adipimide and adipic acid monoamide, is the primary oxidation product.

At sufficient oxygen pressure (when termination proceeds prevalingly as $2 \text{ROO} \cdot \rightarrow \text{ROOR} + \text{O}_2$) and at long kinetic chains, the rate of the initial stage of an initiated oxidation is given by ⁴⁻⁶

$$w_{\text{O}_2} = k_2 k_i^{1/2} k_6^{-1/2} [\text{RH}] [\text{I}]^{1/2} \quad (1)$$

under steady state conditions. In this equation, w_{O_2} is the rate of oxidation, k_2 and k_6 resp. are the rate constant of propagation, or termination resp. and k_i is the rate constant of initiation (defined as $k_i = 2ek_r$, where e is the efficiency of initiation and k_r the rate constant of the monomolecular decomposition); $[\text{RH}]$ resp. $[\text{I}]$ is the concentration of amide resp. initiator.

In order to compare the oxidizability of cyclic amides (*i.e.* monomers of polyamides) and linear amides (models of monomer units in linear polyamides) the initiated oxidation of caprolactam and N-octylbutyramide were investigated. The oxidizability was characterized by the values of $k_2 \cdot k_6^{-1/2}$.

EXPERIMENTAL

Chemicals

Caprolactam, crystallized four times from benzene. N-Octylbutyramide⁷ was purified in the following manner: 200 ml of redistilled amide and 20 ml benzene (purified by sulfonation, extraction with water and distillation) were shaken at room temperature for 5 hours with 25 ml of activated charcoal (0.05–1 mm, heated for 5 hours at 220°C/0.1 Pa) and after filtration pressed by means of argon through a 40 cm column (diam. 1.8 cm) filled with activated aluminium oxide (0.02 to 0.1 mm, heated for 4 hours at 220°C/0.1 Pa). Finally, the amide was distilled *in vacuo* under inert atmosphere, b.p. 150°/53 Pa. 7,7'-Dicumenyl peroxide and 1,1'-azodi(cyclohexanecarbonitrile), crystallized twice from ethanol. 2,2,6,6-Tetramethyl-4-hydroxypiperidine-1-oxyl crystallized twice from the mixture of diethylether + hexane (2 : 1), m.p. 66–70°C. 4,4'-Dimethoxydiphenyl amine crystallized from light petroleum, m.p. 102°C. Oxygen dried with a molecular sieve (4A).

Oxidation

A 5 ml cell containing amide (or lactam) and initiator (for concentrations see Tables) connected by means of a ground joint and a capillary with a thermostated burette (1.5 ml/0.01 ml, or 100 ml/1 ml) was vigorously shaken in a silicone oil bath ($\pm 0.1^\circ\text{C}$) with a frequency 400/min, and the gas volume was read off with an accuracy of 0.3 divisions of the scale.

Analyses

The content of peroxidically bound oxygen in the oxidate was determined iodometrically by potentiometric titration⁷. The contents of acid and imide groups was determined by conductometric titration⁷. The concentration of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl was determined

by HPLC (silanized silica gel, 10 μm , length 30 cm, diam. 4 mm, elution with a 4 : 1 mixture of methanol and water). The gases were analyzed with an Orsat microapparatus, by IR spectroscopy and gas chromatography.

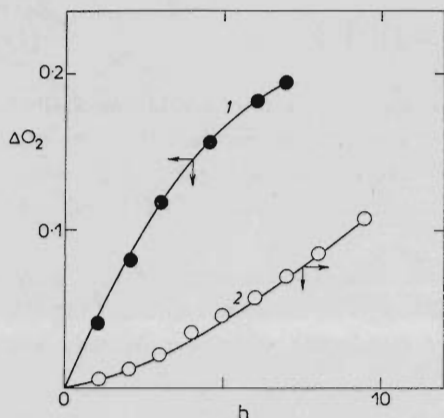


FIG. 1

Oxygen consumption (ΔO_2 , mol kg^{-1}) in the oxidation of caprolactam (90°C): 1 caprolactam + 32.87 mmol/kg 1,1'-azodi(cyclohexanecarbonitrile), 2 caprolactam without initiator, scale right (from the top): 0.02, 0.01. ΔO_2 , mol kg^{-1}

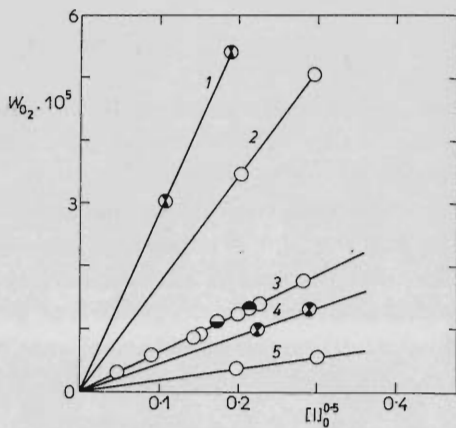


FIG. 2

Dependence of the rate of thermal oxidation of caprolactam (w_{O_2} , mol $\text{kg}^{-1} \text{s}^{-1}$) on the initial initiator concentration $[\text{I}]_0$ 1,1'-Azodi(cyclohexanecarbonitrile): \circ caprolactam in oxygen, \bullet *ibid.* + 1% mol H_2O , \ominus in air; 7,7'-dicumyl peroxide: \otimes caprolactam in oxygen. 1 120°C, 2 100°C, 3 90°C, 4 100°C, 5 80°C

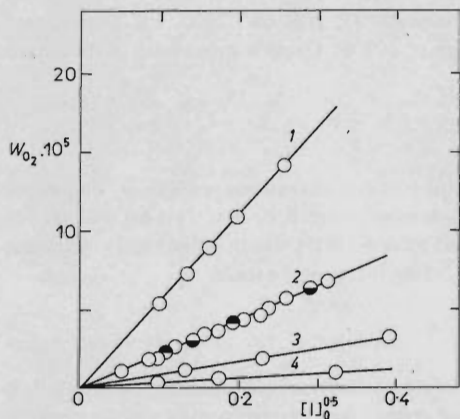


FIG. 3

Dependence of the rate of initiated thermal oxidation of N-octylbutyramide (w_{O_2} , mol · $\text{kg}^{-1} \text{s}^{-1}$) on the initial concentration of 7,7'-dicumyl peroxide $[\text{I}]_0$: \circ oxidation of N-octylbutyramide in oxygen, \bullet *ibid.* + 1% mol H_2O , \ominus in air. 1 130°C, 2 120°C, 3 110°C, 4 100°C

RESULTS AND DISCUSSION

The autooxidation of caprolactam was autocatalytic, in accordance with linear N-alkylamides^{4,7}, and its rate was negligible as compared with the rate of the initiated oxidation (Fig. 1).

Up to oxygen consumptions of 30 mmol/kg of amide, the dependence of the oxygen consumption on time was always linear and all consumed oxygen was peroxidically bounded in the liquid reaction product (Table I). Only at oxygen consumptions higher than 30 mmol/kg a fraction of consumed oxygen was present as imide or carboxyl groups. With the given accuracy of analytical methods, gaseous products (CO₂ and traces of CO and H₂) were detected only at oxygen consumptions higher than 100 mmol/kg.

TABLE I

Initiated oxidation of caprolactam: oxygen consumption (ΔO_2) and contents of peroxidic (P), acid (A) and imide (D) groups in products

T °C	$[I]_0$ mmol kg ⁻¹	t min	ΔO_2	[P]	[A]	[D]
				mmol kg ⁻¹		
90	0	1 440	30.0	28.0	0	0
I = 1,1'-Azodi(cyclohexanecarbonitrile)						
80	38.7	60	14.5	15.0	0	0
80	77.2	60	18.7	18.2	0	0
90	1.9	90	15.7	14.4	0	0
90	8.2	150	51.4	48.1	0	0
90 ^a	21.3	150	69.6	69.6	0	17.3
90 ^b	41.5	90	65.3	54.1	0	13.0
90	41.7	90	63.2	54.2	0	9.8
90	41.9	180	128.7	110.7	0	28.1
90	79.6	60	59.5	58.1	0	3.0
90	32.9	1 320	285.0	91.8	178.0	54.0
100	41.0	30	55.9	48.9	0	9.8
100	87.2	15	38.6	33.6	0	9.7
I = 7,7'-Dicumenyl peroxide						
100	49.6	60	34.3	30.2	0	0
100	83.9	50	37.2	34.0	0	1.5
120	34.6	95	213.0	153.0	23.0	50.7

^a With 1% mol H₂O. ^b In air.

Hence, the rate of oxidation was determined from measurements of volume changes up to consumption of oxygen of 30 mmol/kg. Oxidations at atmospheric pressure proceeded with the same rate both in oxygen and air (Figs 2 and 3) so that between 20 and 100 kPa the reaction rate is not affected by changes of oxygen pressure. Also, it was verified that the rate of oxidation remained unaffected by traces of moisture, because even the presence of 0.01 mol H₂O/mol amide did not affect the rate of oxidation (Figs 2 and 3).

Kinetics of the initial stage of initiated thermal oxidation

The dependence of the oxidation rate w_{O_2} on the square root of the initiator concentration and independence on the oxygen pressure prove that the initial stage of the initiated thermal oxidation of caprolactam and N-octylbutyramide is a chain reaction with the predominant interaction of two peroxyradicals in the termination step (Figs 2, 3). Thus, the thermal oxidation of caprolactam initiated with 1,1'-azodi(cyclohexanecarbonitrile) or 7,7'-dicumenyl peroxide, as well as that of N-octylbutyramide initiated with 7,7'-dicumenyl peroxide is controlled by Eq. (1), as has

TABLE II

Oxidation of caprolactam and N-octylbutyramide initiated with 7,7'-dicumenyl peroxide or 1,1'-azodi(cyclohexanecarbonitrile)

T °C	$k_2(k_i/k_6)^{1/2} \cdot 10^5$ $\text{kg}^{1/2} \text{mol}^{-1/2} \text{s}^{-1}$	E kJ/mol	A	$k_2k_6^{-1/2} \cdot 10^3$ $\text{kg}^{1/2} \text{mol}^{-1/2} \text{s}^{-1/2}$
Caprolactam + 1,1'-azodi(cyclohexanecarbonitrile)				
80	0.22			0.92
90	0.70	119	$1.1 \cdot 10^{11}$	1.50
100	1.94			2.24
Caprolactam + 7,7'-dicumenyl peroxide				
100	0.50			3.11
120	3.33	117	$1.1 \cdot 10^{11}$	6.71
N-Octylbutyramide + 7,7'-dicumenyl peroxide				
100	0.58			3.74
110	1.63			5.89
120	4.29	122	$7.2 \cdot 10^{11}$	9.06
130	11.00			13.60

been found also for other linear N-alkyl amides^{4,5}. The values of $k_2 \cdot k_i^{1/2} \cdot k_6^{-1/2}$ are summarized in Table II, which moreover contains the values of overall activation energies $E = E_2 + 1/2E_i - 1/2E_6$ and pre-exponential factors calculated using the Arrhenius equation.

The rate constants of initiation reactions for 7,7'-dicumenyl cumyl peroxide were calculated from the equation⁸ $\log k_r = 13.180 - 134 \text{ kJ mol}^{-1}/19.14 \text{ T}$. The applicability of this relation (valid for chlorobenzene solutions of 7,7'-dicumenyl peroxide) for the amide medium was verified for the thermal oxidation of N-octylbutyramide initiated with 7,7'-dicumenyl peroxide at 120°C in the presence of 4,4'-dimethoxydiphenyl amine used as scavenger. Assuming the stoichiometric factor (f) is equal 2, the rate constant k_i was calculated from the relation⁶ $\tau = f[S]_0/k_i[I]_0$ (where τ is induction period, $[S]_0$ and $[I]_0$ respectively are the initial concentrations of the scavenger and 7,7'-dicumenyl peroxide) as $(2.4 \pm 0.2) \cdot 10^{-5} \text{ s}^{-1}$ (Table III). This value proves that the rate of the decomposition of 7,7'-dicumenyl peroxide in the amide medium is virtually identical with that observed in chlorobenzene⁸ ($2.46 \cdot 10^{-5} \text{ s}^{-1}$), n-decane⁹ ($2.28 \cdot 10^{-5} \text{ s}^{-1}$) and cumene¹⁰ ($2.84 \cdot 10^{-5} \text{ s}^{-1}$).

TABLE III

Thermal oxidation of N-octylbutyramide at 120°C initiated with 7,7'-dicumenyl peroxide (I) in the presence of 4,4'-dimethoxydiphenyl amine (S)

$[I]_0$, mmol kg ⁻¹	$[S]_0$, mmol kg ⁻¹	τ , min	k_i , s ⁻¹
3.53	2.26	88 ± 8	$(2.42 \pm 0.23) \cdot 10^{-5}$
3.53	1.14	47 ± 2	$(2.32 \pm 0.13) \cdot 10^{-5}$

TABLE IV

Thermolysis of 1,1'-azodi(cyclohexanecarbonitrile) (I) in caprolactam in the presence of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (\dot{R}). Symbols $[\dot{R}]_0$ or $[\dot{R}]_t$, resp. refer to initial concentrations of \dot{R} or concentrations of \dot{R} after t min of reaction

T °C	$[I]_0$ mmol kg ⁻¹	$[\dot{R}]_0$ mmol kg ⁻¹	t min	$[\dot{R}]_t$ mmol kg ⁻¹	k_i 10^5 s^{-1}	k_r 10^5 s^{-1}	e
80	81.2	44.2	570	29.6	0.60	0.84	0.36
90	43.0	37.6	180	28.8	2.20	3.10	0.36
100	97.5	38.6	35	25.0	7.50	10.40	0.35

The rate constants of initiation reactions for 1,1'-azodi(cyclohexanecarbonitrile) were measured using its thermolysis⁶ in caprolactam in the presence of a stable radical, 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (Table IV). From the k_i values thus obtained and values of k_r calculated for 1,1'-azodi(cyclohexanecarbonitrile) in chlorobenzene solution using the equation¹¹ $\log k_r = 15.490 - 139 \text{ kJ mol}^{-1} / 19.14 T$, the value of the efficiency of initiation e was found 0.36 (Table IV).

The results given above were used in calculating the parameters of oxidizability $k_2 \cdot k_6^{-1/2}$ (Table II). The oxidizability of caprolactam, *i.e.* of the cyclic amide, and of linear N-octylbutyramide appeared to be close to each other and comparable with published data for other amides ($k_2 \cdot k_6^{-1/2}$ for N-propionyl propylamide⁴ at 116°C was $4.9 \cdot 10^{-5}$ and for dimethyl acetamide¹² at 90°C $1.49 \cdot 10^{-5} \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \text{ s}^{-1/2}$).

REFERENCES

1. Dege G. J., Reimschuessel H. K.: *J. Polym. Sci., Chem. Ed.* **11**, 873 (1973).
2. Šebenda J., Lánská B.: *Symposium on Macromolecules, Preprints*, Vol. I, p. 669. Mainz 1979.
3. Rieche A., Schön W.: *Kunststoffe* **57**, 1, 49 (1967).
4. Sagar B. F.: *J. Chem. Soc. B*, 1967, 428, 1047.
5. Pozdeeva N. N., Sapatchova T. I., Aleksandrov A. L.: *Izv. Akad. Nauk USSR, Ser. Khim.* 1976, 1738.
6. Emanuel N. M., Denisov E. T., Maizus Z. K.: *Cepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoi Faze*. Nauka, Moscow 1965.
7. Šebenda J., Postnikov L. M., Lánská B.: *This Journal* **40**, 1877 (1975).
8. Ivanchenko P. A., Charitonov V. V., Denisov E. T.: *Vysokomol. Soedin. IIA*, 1622 (1969).
9. Antonovskii V. L., Bezborodova L. D.: *Zh. Fyz. Khim.* **44**, 1244 (1970).
10. Bailey H. C., Godin G. W.: *Trans. Faraday Soc.* **52**, 68 (1956).
11. Chin-hua S. Wu., Hammond G. S., Wright J. M.: *J. Amer. Chem. Soc.* **82**, 5386 (1960).
12. Sapatchova T. I., Agliullina G. G., Aleksandrov A. L.: *Neftekhimiya* **14**, 450 (1974).