EFFECT OF ADDITIVES AND IMPURITIES ON THE INITIAL STAGE OF THERMAL OXIDATION OF N-OCTYLBUTYRAMIDE

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It has been proved that complications involved in the kinetic expression of the oxidation of N-alkylamides described in the literature are due to the effect of some impurities present in the substrate. Octylamine appeared to be the inhibitor of oxidation; on the other hand, however, its oxidation products initiated the oxidation of N-octylbutyramide. The accelerating effect of the oxidation products of amine on the oxidation of alkylamide becomes operative through the presence of a small (less than 0·5 mmol/kg) amount of carboxylic acid. Typical kinetic features of branched chain reactions were observed in the oxidation of N-octylbutyramide, namely, nonlinear consumption of the inhibitor and the existence of its critical concentration. The autoxidation kinetics of N-octylbutyramide can be described in terms of a simple scheme of a degenerated chain reaction with one intermediate product.

Sagar's papers[1-3] have shown that the autoxidation of N-alkylamides proceeds on the carbon atom of the methylene group adjacent to the nitrogen atom, with hydroperoxides as the primary oxidation products. According to Sagar, the formation of hydroperoxides is an autocatalytic radical reaction with an induction period; in the region of the latter the rate of oxidation is proportional to the square root of the concentration of hydroperoxides. The hydroperoxides formed are thermally decomposed prevailingly *via* a nonradical route to yield N-acylamide, N-formylamide, amide (corresponding to the acyl moiety of N-alkylamide), and aldehyde (corresponding to the alkyl moiety); the latter is then oxidized with formation of carboxylic acid with the same number of carbon atoms. At a low extent of oxidation (c. 5%) the concentration of hydroperoxides passes through a maximum which is attributed to the formation of inhibiting products[3]. However, not one of the oxidation products proven in the mixture exhibited inhibition effect in the model experiment. Primary amines and isocyanides, which have not been found among the oxidation products, acted as effective inhibitors of oxidation[3].

The inhibitive effect of amines in the oxidation of amides seems surprising, because it is known from the behaviour of linear polyamides that terminal amino groups act just in an opposite manner, that is, they accelerate changes occurring during the degradation[4]. The overall kinetics of thermal oxidation, which according to Sagar is a degenerated branched chain reaction with a non-chain consumption of the branching product, is very sensitive to slight interferences with the elementary

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processes[5]. We therefore decided to study the initial stage of the thermal oxidation of N-octylbutyramide with a special emphasis on the purity of amide while trying to elucidate facts so far unexplained, and above all to find and identify the inhibitor of oxidation, if any. This finding would be of considerable importance for the possibility of influencing the degradation behaviour of polyamides.

EXPERIMENTAL

N-*Octylbutyramide* (I). To a solution of 212 g (1·64 mol) of octylamine (99·8%) in 1 l of ether, 87·35 g (0·82 mol) of butyryl chloride (99·9%) diluted with 50 ml of ether was added with stirring at 4—7°C during 2 h. Then a solution of 80 g NaOH in 500 ml water was added with cooling, after which the other half of the required amount of butyryl chloride (87·35 g) was added at 4—7°C during 30 min. The ether layer was washed four times with 100 ml of saturated aqueous NaCl solution; after evaporation of ether at reduced pressure amide *I* (310 g) was redistilled in an inert atmosphere at 143°C/1·8 Torr. The main fraction (250 g) obtained after separation of 7 g of the forerun was redistilled into several fractions (*I*/1—*I*/12 *cf.* Table II), which were analyzed and kept, before oxidation, in the dark in an inert atmosphere; neither peroxides nor hydroperoxides were detected iodometrically in any of the fractions of amide *I*.

N-*Propylpropionamide*. Amide prepared according to ref.[1] was redistilled in an inert atmosphere, b.p. 65°C/0·5 Torr. According to gas chromatography it contained 0·05% of impurities; the content of bases determined conductometrically was 2·1 mmol/kg.

Octylammonium laurate. In 5 ml of light petroleum 218 mg (1·69 mmol) of octylamine (99·8%) and 337 mg (1·67 mmol) of lauric acid (m.p. 43·5°C) were heated to 35°C. The solution was then cooled to 0°C; the crystals were filtered off, washed with 2 ml of light petroleum and dried at 25°C/0·1 Torr. The yield was 391 mg (70% theor.) of salt, m.p. 49—50·5°C, with the neutralization coefficient with respect to the acid as well as base corresponding to theory.

Oxidation

The vessels used were purified with chromic acid and thoroughly washed with distilled water. All experiments were carried out while trying to observe strictly the same conditions, thus allowing a reproducibility of formation of the main products of ±5% to be attained.

Oxidation in ampoules. Amide *I* (0·8—1·5 g) and a given amount of the respective additive (if needed) were placed in an ampoule (12—16 ml in volume) which was then connected through a three-way cock with a 50 ml gasometer burette with mercury used for sealing. After cooling to −10°C the ampoule was alternately evacuated and filled with oxygen (96%); on cooling with liquid nitrogen, a measured volume of oxygen (48 ml in most cases) was introduced into the ampoule. The neck of the ampoule was sealed off in a place narrowed in advance. The ampoules were rotated perpendicular to their axis (30 r.p.m.) in a silicone bath at 120°C for a given time.

Oxidation with measurements of a change in volume of the gas phase. Amide *I* (approx. 1·7 g) was placed in an oxidation cell (6 ml in vol.) provided with a side tube and capillary; the side arm was then sealed off, the cell was connected with the gasometer burette (1·5/0·003 ml or 10/0·02 ml) and the apparatus was filled with oxygen (96%). The cell was thermostated to 120°C (with stirring) and the burette was thermostated to 30°C.

After 3 h of the oxidation of amide *I* the IR spectra of the gas phase (Perkin-Elmer 621, 10 cm cell) exhibited no characteristic frequencies for carbon dioxide, carbon monoxide, water, and

ammonia. After oxidation for 5—10 h there was only a hint of the presence of carbon dioxide. Only after 100 h of oxidation carbon dioxide was present in a measurable amount, while carbon monoxide was present in traces only. Thus, in the first hours of oxidation volume changes of the gas phase equalled the consumption of oxygen.

The experiment at 140°C was carried out in a 20 ml cell with 8·5 g of amide *I*/1 and with a 50/0·1 ml burette. The contents of O_2, CO_2, and CO were determined after 10—20 h intervals in 10 ml samples with an Orsat microapparatus (burette 10/0·1 ml). No other compounds (H_2, C_nH_m, RNH_2) were detected in the gases (IR, GLC). The samples were removed from the apparatus into evacuated syringes (50 ml) and then a known amount of oxygen was introduced into the apparatus. The consumption of oxygen was calculated from the volume of the gaseous products and from changes in the volume of the gas phase.

The samples after oxidation were stored in sealed ampoules at —79°C. All analyses were completed within 48 h after the oxidation at the latest; it was verified that during this time there had been no changes in composition of the samples.

Analysis of Reaction Products

Peroxides or hydroperoxides[6]. The sample (0·2—0·8 g) was dissolved under a CO_2 atmosphere in 15 ml of a saturated 2-propanolic solution of potassium iodide. After addition of 0·75 ml of acetic acid the solution was heated to 40°C for 30 min in a CO_2 atmosphere. Iodine was titrated in a nitrogen atmosphere with a 0·01M aqueous solution of sodium thiosulphate with a Potentiograph Metrohm E 336 apparatus by using a platinum and a calomel electrode. The blank test was determined from 3—4 titrations of different amounts of the same sample (the ratio of weighed amounts being 1 : 2 : 3 : 4). The blank test value of the medium was 0·25 μmol at utmost and amounted as a rule to less than 10% of the amount of peroxides found in the samples. The experimental error was 0·3 mmol/kg.

Bases, acids, and diacylamines. A conductometric titration in the 2-propanol–water mixture was used. Samples (10—200 mg) were dissolved in 9 ml of 2-propanol (redistilled with Na_2CO_3) and 3 ml of water; solvents and titration agents were stored under nitrogen, and dissolution, titration, and hydrolysis were carried out in nitrogen. The bases were titrated with 0·1M aqueous HCl solution; the blank test was less than 0·1 μmol and the error of determination was 0·1 mmol/kg. The smallest detectable amount of the bases, also in the form of a salt with the carboxylic acid, was 0·1 mmol/kg. The acid content was determined in the same medium by titration of 10—200 mg of the sample with 0·1M propanolic solution of sodium propoxide. The blank test of the medium was 0·15—0·20 μmol and the error of determination was 0·2 mmol/kg. The limit of perception of acids, also in the form of a salt with the amine, was 0·2 mmol/kg. After the titration of acids had been completed, a solution of sodium propoxide was added in a two- or threefold amount of the expected content of the hydrolyzable groups. On heating to 40°C/20 min the excess of the strong base and the content of the weak bases were determined by titration with a 0·1M aqueous HCl. The content of hydrolyzable groups corresponding to the content of diacylamines was calculated from the content of weak bases after the content of acids and bases (determined by separate titrations) and the blank test had been subtracted. The blank test was 0·5—1·8 μmol; since the error of determination of acids and bases was reflected in the determination of diacylamines, the error of determination of diacylamines was 1 mmol/kg. Water was determined in the samples by titration with K. Fischer reagent with an accuracy of 4 mmol/kg.

Carboxylic acids and amides. Chromatographic analyses were performed with a Perkin-Elmer F 11 apparatus with a FID detection and with nitrogen (50 ml/min) as the carrier gas. A 1 m column was used packed with a 5% poly(ethylene adipate) on Chromosorb W, column temperature

80–100°C, 8 K/min. The acids were identified on the basis of the elution times of authentic samples.

Octylamine. The compound was determined chromatographically on a 1 m column with 5% Carbowax 2 M on Chromosorb W impregnated with 5% sodium methanilate at a column temperature of 80–190°, 8 K/min. The limit of perception for octylamine was 0·1 mmol/kg.

RESULTS AND DISCUSSION

Main Products in the Initial Stage of the Thermal Oxidation of N-*Octylbutyramide*

A comparison of the photoxidation[7] (at 35°C) and thermal oxidation (at 140°C) of N-alkylamides has revealed that thermal oxidation proceeds much milder (Table I). During the thermal reaction 1 mol of oxygen was consumed by the oxidation of 1 mol of N-octylbutyramide (*I*), while the photooxidation of a related N-butylhexanamide (*II*) initiated at 35°C with UV light required 2·5 times more oxygen, and a greater number of products were formed at the same time.

In accord with Sagar's results, the initial stage of the oxidation of *I* at 120°C proceeded with formation of hydroperoxides, diacylamines, and acids. Since during the first 5–10 h of oxidation virtually no gaseous products were formed, the changes in the gas phase volume were equal to the oxygen consumption. Roughly 90% of con-

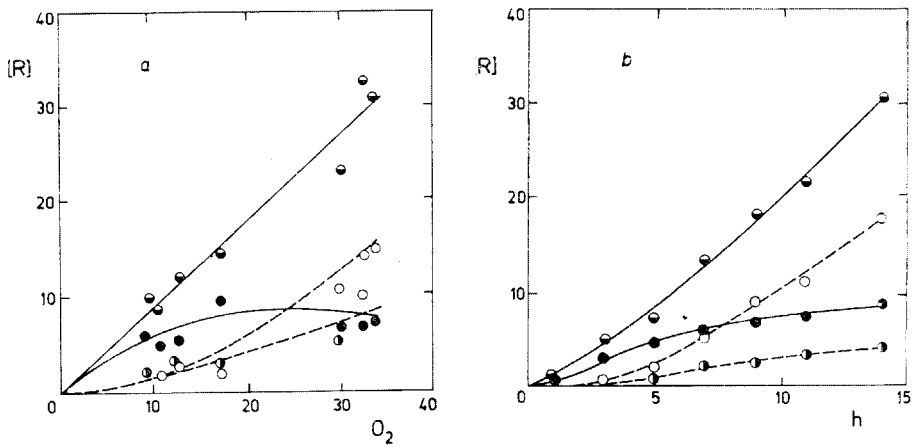

FIG. 1

Formation of Main Products (R) in the Oxidation (120°C) of Amide *I*/4 in a Cell with an Attached Burette (*a*, $p(O_2)$ = 735 Torr) and of Amide *I*/9 in Sealed Ampoules (*b*, $p(O_2)$ = 7 atm)
a) [R] (mmol/kg) as a function of the oxygen consumption (mmol/kg), *b*) time dependence of [R]; R: ● peroxides, ○ acids, ◑ diacylamines, ◒ sum of peroxides + acids + diacylamines.

sumed oxygen were present in hydroperoxides, diacylamines, and acids (Fig. 1*a*). According to gas chromatography, a number of the other products were also formed in small quantities; of these, butyramide and octylamine were determined. Amines were obviously present in the oxidation products in the form of salts with carboxylic acids.

Oxidation in a Cell and in Sealed Ampoules

The rate of oxidation measured from the volume of consumed oxygen greatly depended on the intensity of stirring. There was also a justified concern that some of products which may then affect the rate of oxidation might be distilled off during the reaction[8]. The reaction was therefore studied in sealed ampoules. The volume of the ampoules was so large that the amount of amide used at a given temperature formed during rotation of the ampoules a film (c. 0·5 mm thick) on their walls. Nevertheless, the reaction somewhat depended on the oxygen pressure:

$p(O_2)$, atm:	1	4	7	9
Peroxides, mmol/kg:	5·0	8·0	10·1	9·5.

All experiments were therefore carried out at oxygen pressure of 6–7 at. The process of oxidation in the ampoules did not differ as to its character from oxidation in a cell with an attached burette (Figs 1*a*,*b*).

Effect of Impurities

The oxidation of the comparatively pure fraction *I*/9 (Fig. 1*b*) proceeded differently from the published results[3]. The time dependence of the formation of hydroperoxides

TABLE I

Oxygen Consumption (ΔO_2) and Formation of Diacylamines (D), Acids (A), Water, Carbon Dioxide and Carbon Monoxide in the Oxidation of N-Octylbutyramide (*I*) at 140°C and in Photooxidation of N-Butylhexanamide[7] (*II*) at 35°C

Concentration in mol/mol of consumed alkylamide.

Amide	ΔO_2	[D]	[A]	[H_2O]	[CO_2]	[CO]
I	1·00	0·09	0·34[a]	0·54	0·14	0·08
II	2·55	0·20	0·43[b]	2·00	0·57	0·54

[a] The prevailing amount of acids consisted of butyric acid (0·16 mol) and octanoic acid (0·13 mol). [b] All acids (from C_1 to C_6) were formed in approximately the same amounts.

TABLE II

The Content of Peroxides (P), Diacylamines (D), Acids (A) and Bases (B) after the Oxidation of Different Fractions of N-Octylbutyramide (*I*) at 120°C

Concentration in mmol/kg. OA octylamine, $S = [P] + [D] + [A]$.

I	Impurities			After oxidation				
	[A]	[B]	[OA]	[P]	[D]	[A]	[B]	*S*
				Reaction time: 3 h				
I/1	—	3·1	0·9	11·0	4·0	3·5	1·0	18·5
I/2	—	22·0	3·6	13·5	31·0	3·4	3·0	47·9
I/3	<0·2	3·9	<0·1	4·1	0	2·7	0	6·8
I/4	<0·2	4·1	<0·1	0·6	0	3·2	0	3·8
I/5	<0·2	0·7	<0·1	4·0	1·4	0·8	1·0	6·2
I/6	0·5	11·6	—	29·4	22·8	2·5	2·9	54·7
I/7	0·3	1·7	—	8·0	2·0	2·0	1·0	12·0
I/8	1·4	1·6	—	4·6	2·3	4·0	1·0	10·9
				Reaction time: 5 h				
I/9	<0·2	0·7	<0·1	3·2	0·6	0·4	1·0	4·2
I/9	<0·2	0·7	<0·1	4·5	1·8	1·0	1·0	7·3
I/10	—	6·1	—	18·4	21·8	7·9	2·4	48·1
I/11	—	1·5	—	12·0	4·8	2·0	0·7	18·8
I/12	—	0·7	—	6·6	1·6	1·0	1·0	9·2

did not exhibit a maximum which was observed by Sagar for the oxidation of N-propylpropionamide[3] at 131°C. The amide fraction *I*/9 was oxidized rather slowly, exhibiting the usual S-shaped course, as could be expected from an analogy with the oxidation of *e.g.* alkanes which at 120°C practically remain unoxidized, or with the oxidation of amines and their derivatives. Amines are oxidized the slower the higher their ionization potential; with respect to the high ionization potential of amides[9], a low rate of oxidation could be expected. However, the rates of oxidation of the individual fractions of *I* differed considerably from each other (Table II). In the oxidation of fraction *I*/1 a maximum was found on the curve of the formation of hydroperoxides, similarly to N-propylpropionamide which was oxidized for the sake of comparison with paper[3] (Fig. 2). The results prove that the maximum of the concentration of hydroperoxides is not characteristic of the oxidation of N-alkylamides, but that it is obviously due to some compound present as an impurity in the amide under investigation. Also Sagar's explanation of the slowing-down of oxidation owing to the inhibitive effect of some of the oxidation products was not con-

firmed; the oxidation of amide *I*/1 in the presence of a small amount of its oxidation product proceeded much faster than for the original amide *I*/1 alone (Table III).

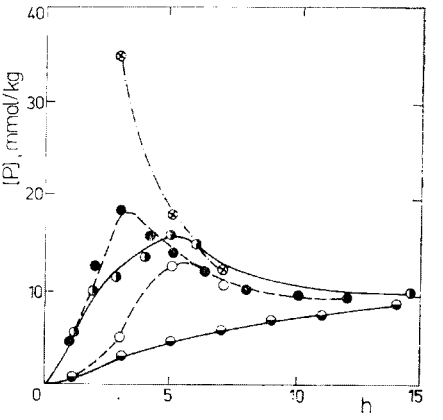

FIG. 2

Formation of Peroxides (P) in the Oxidation of Amides at 120°C and $p(O_2)$ 7 atm

◒ Amide *I*/9, ○ amide *I*/9 + 19·4 mmol/kg of octylamine, ◑ amide *I*/1, ● amide *I*/1 + + 20·0 mmol/kg of octylamine, ⊗ N-propylpropionamide.

TABLE III

The Effect of Additives on the Relative Yield of Peroxides, Diacylamines, and Acids in the Oxidation of N-Octylbutyramide (*I*/1) at 120°C (3 h)

Meaning of A, D, P, *S cf.* Table II; Q_P (or Q_D, Q_A, Q_S respectively) is $[P_a]/[P]$ (or $[D_a]/[D]$, $[A_a]/[A]$, S_a/S respectively) where the values without an index correspond to the yield of oxidation of amide *I*/1 and those with the index a are related to the oxidation of the same amide in the presence of additive.

Additive	%	Q_P	Q_D	Q_A	Q_S
$C_3H_7CONH_2$	2·34	1·3	0·8	1·1	3·2
$(C_3H_7CO)_2NH$	2·72	1·2	1·0	0·8	3·0
$C_7H_{15}CHO$	3·81	2·4	4·3	43·0	49·7
$C_7H_{15}CHO + C_3H_7CONH_2$	3·83 + 2·48	2·6	—	—	—
$C_7H_{15}CHO + C_8H_{17}NH_2$	3·97 + 2·70	1·1	80·0	5·3	86·4
H_2O	2·27	1·0	1·0	1·0	3·0
$C_6H_5NH—C=N—(CH_2)_5$	0·22	0·1	1·5	1·0	2·6
$C_3H_7CH=N—C_4H_9$	0·84	1·4	2·0	10·0	13·4
$C_7H_{15}—CH=C(C_6H_{13})—CH=N—C_8H_{17}$	0·37	3·3	2·0	21·0	26·3
Oxidation product of amide *I*/1[a]	2·50	5·7	8·6	13·0	27·3
Cu acetoacetonate	0·01	4·2	0	152·0	156·2
Cu acetoacetonate + $C_8H_{17}NH_2$	0·01 + 1·46	0	1·0	1·1	2·1
Stabilin 9[b]	0·76	0·1	0	0	0·1

[a] Reaction time 100 h at 120°C. [b] Commercial stabilizer produced in the U.S.S.R.

The inhibitive effect of diacylamine observed in the oxidation of ε-caprolactam[10] has not been confirmed either (Table III).

Effect of Amines and Carboxylic Acids

The individual fractions of amide *I* were characterized mainly by their base content (Table II). It can be seen from the results that the rate of oxidation of the given frac-

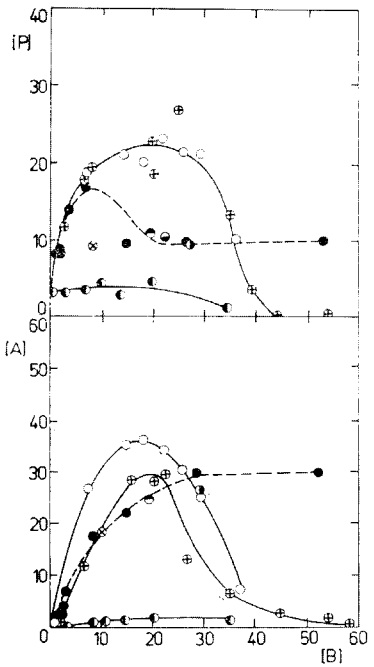

FIG. 3

Formation of Peroxides (P) and Acids (A) in the Oxidation of Amide *I* at 120°C and $p(O_2)$ 7 atm in the Presence of Bases (B) and Further Additives

[P], [A], [B], and additions of lauric acid (LA) are given in mmol/kg. Starting material: ● *I*/8, ⊕ *I*/1, ○ *I*/9 + LA (3·9), ◓ *I*/9 + LA (24·3), ◒ *I*/1 + LA (30·8), ◑ *I*/8 + LA (68·3), ⊗ *I*/4 + LA (14·3), ◐ *I*/9; to the fractions *I*/1, *I*/4, and *I*/9 (*cf.* Table II) octylamine was added, to fraction *I*/8 octylammonium laurate was added.

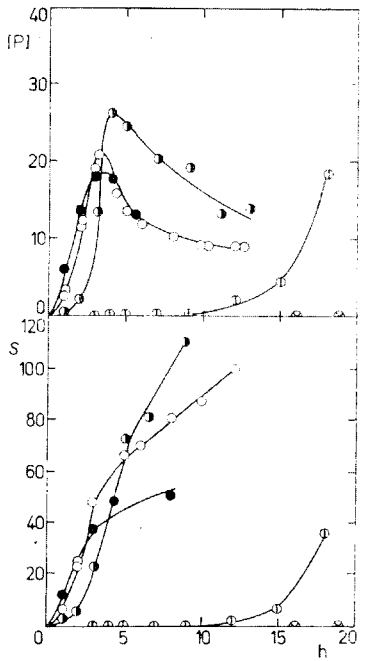

FIG. 4

Oxidation of Amide *I*/1 at 120°C and $p(O_2)$ 7 atm in the Presence of Octylamine (OA)

P peroxides, D diacylamines, A acids; S = [P] + [O] + [A] (in mmol/kg). [OA], mmol/kg: ● 6·7, ○ 20·0, ◑ 35·0, ◌ 56·0, ⊗ 75·0.

tion is related to the base content. However, the relationship is obviously not a simple proportionality. Thus, for instance, the oxidation of fraction *I*/9 with octylamine added proceeded differently from the oxidation of fraction *I*/1 with the same content of octylamine (Fig. 2). The fact that the difference in the rates of oxidation of these two fractions is not due to the different overall base content or to the different content of specifically bonded octylamine was even more stressed by the results of the oxidations of both fractions with various amounts of added octylamine (Fig. 3).

The most probable impurities present in N-octylbutyramide are amines and acids. The addition of lauric acid (dodecanoic acid) in an amount of 3·9 mmol/kg to fraction *I*/9 did not affect the rate of oxidation. However, the same small amount of acid brought the rates of oxidation of both fractions *I*/1 and *I*/9 closer to each other depending on the amount of octylamine added (Fig. 3). Consequently, an acceleration of the oxidation of pure amide requires a simultaneous presence of small amounts of carboxylic acid and amine. A similar effect on the rate of oxidation of the purer fraction of amide *I* was exhibited by an addition of the octylammonium salt of lauric acid in an amount up to 5 mmol/kg (Fig. 3). The effect of other impurities present in amounts imperceptible to us cannot be ruled out either.

Additions of higher amounts of octylamine to amide *I*/1 (or to a mixture of amide *I*/1 and 3·9 mmol/kg of lauric acid) slowed down the oxidation (Figs 3, 4). The time dependence of the oxidation of amide *I*/1 with various amounts of octylamine added revealed that amine has a distinct inhibitive effect on the oxidation of amide (Fig. 4). Under the reaction conditions amine is obviously oxidized itself, and some of its oxidation products then accelerate the oxidation of amide. Such active products could be *e.g.* aldimines (Table III), which are primary oxidation products of primary amines[11], or condensation products of aldimine (Table III) which arise very fast on heating the latter[12].

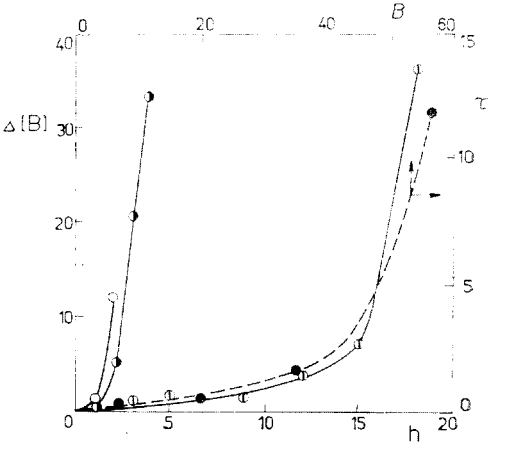

FIG. 5

Decay of Bases, Δ[B] (mmol/kg), and the Induction Period, τ(h), in the Oxidation of Amide *I*/1 in the Presence of Octylamine (OA)

Meaning of [B] *cf.* Fig. 3, ——— Δ[B], ------- τ; [OA], mmol/kg: ● 6·7, ○ 20·0, ◑ 35·0, ⊕ 56·0.

The consumption of octylamine as the inhibitor of the oxidation of N-octylbutyramide is nonlinear. The amine concentration starts decreasing only toward the end of the induction period of amide oxidation, the length of which depends on the initial concentration of amine (Fig. 5). The time needed for the formation of 2·5 mmol of hydroperoxide/kg was regarded as the induction period of the oxidation of *I*. The character of the dependence of the length of the induction period on the initial amine concentration (Fig. 5) indicates the existence of a critical amount of the inhibitor.

At a ratio of carboxylic acid to amine equal or higher than unity or in the presence of amine as an ammonium salt of the carboxylic acid (in a concentration above 30 mmol/kg) the inhibitive effect of amine is reduced (Fig. 3).

The Reaction Mechanism

The character of oxidation of comparatively pure fractions of N-octylbutyramide, nonlinear consumption of the inhibitor, and the existence of a critical concentration of the inhibitor are typical of branched chain reactions. For degenerated chain reactions with a single intermediate product it holds that the maximal rate of oxidation is given by[5]

$$\left(\frac{\mathrm{d}\sum[\text{products}]}{\mathrm{d}t}\right)_{\max} = \frac{k_2^2 k_3}{k_6 k_M}[\text{amide}]^2\,, \qquad (1)$$

where k_2 is the constant of propagation of the chain of the autoxidation reaction, k_6 is the constant of chain termination, k_3 is the decomposition constant of peroxide into radicals, and k_M is the constant of nonradical decomposition of peroxide. By substituting experimental values from the oxidation of amide *I*/9 (Fig. 1*b*) and using Sagar's value[3] $k_3/k_M = 0{\cdot}03$ we obtain $k_2/k_6^{0{\cdot}5}$ of the order of magnitude of 10^{-3} $(\mathrm{l/mol\,.\,s})^{0{\cdot}5}$. Although the estimate is very rough, the value is still in fair agreement with the published values obtained in the initiated oxidation of N-alkylamides[3,13].

Nonlinear consumption of the inhibitor occurs under such conditions where the formation of the branching intermediate has not been completely suppressed by the inhibitor and where the intermediate, hydroperoxide in this case, is the main initiator of chains. Critical phenomena take place on such occasions when the rate of formation of hydroperoxides *via* the degenerated chain reaction equals the rate of decay of hydroperoxides from the oxidized system. By increasing the inhibitor concentration the formation passes from an autocatalyzed to a stationary regime. Assuming that the inhibitor terminates two chains we have[5]

$$[\text{amine}]_{\text{crit}} = k_2 k_3/(k k_7[\text{amide}])\,, \qquad (2)$$

where $k = k_3 + k_M$ and k_7 are the rate constants of chain termination by the inhibitor, amine in this case. Substitution of experimental values gives k_2/k_7 roughly equal to 0·2. The latter value is not characteristic of strong inhibitors, but if one takes into account the low participation of homolytic cleavage in the overall decomposition of hydroperoxides[3], then this value is not at variance with the observed inhibitive effect of amines. It cannot be excluded however that the inhibition process also involves some other compounds present in traces only.

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