OXIDIZABILITY AND STRUCTURE OF LACTAMS

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The radical-initiated chain oxidation of five- to nine-membered lactams with molecular oxygen has been studied by the quantum-chemical method AM1. It has been confirmed that the reaction is controlled by its propagation step. The kinetic length of the oxidation chains correlates with the energy of formation of the lactam radical by abstraction of hydrogen from the methylene group adjacent to nitrogen atom. With five- to eight-membered rings the reaction is symmetry-forbidden.

The oxidation of lactams with molecular oxygen is a radical chain reaction taking place predominantly at the carbon atom of methylene group adjacent to nitrogen[1,2]. In the steady state, i.e. at a constant concentration of radicals, the oxidation of the lactams (LH) initiated with an azo compound (R–N=N–R) proceeds according to Eqs (*1*) – (*5*):

$$\mathrm{R{-}N{=}N{-}R} \longrightarrow 2\,\mathrm{R^{\bullet}} + \mathrm{N_2} \xrightarrow{\mathrm{O_2}} \mathrm{ROO^{\bullet}} \qquad \text{radical formation} \qquad (1)$$

$$\mathrm{LH} + \mathrm{ROO^{\bullet}} \xrightarrow{v_i} \mathrm{L^{\bullet}} + \mathrm{ROOH} \qquad \text{initiation} \qquad (2)$$

$$\mathrm{L^{\bullet}} + \mathrm{O_2} \xrightarrow{k_0} \mathrm{LOO^{\bullet}} \qquad \text{oxidation} \qquad (3)$$

$$\mathrm{LOO^{\bullet}} + \mathrm{LH} \xrightarrow{k_p} \mathrm{LOOH} + \mathrm{L^{\bullet}} \qquad \text{propagation} \qquad (4)$$

$$2\,\mathrm{LOO^{\bullet}} \xrightarrow{k_t} \text{imide} + \mathrm{H_2O_2} \qquad \text{termination} \qquad (5)$$

where L$^{\bullet}$ is the radical formed from the lactam LH by the abstraction of hydrogen atom from the methylene group adjacent to nitrogen, LOO$^{\bullet}$ is the corresponding peroxy radical, and LOOH is the lactam hydroperoxide.

The radicals R$^{\bullet}$ are generated by decomposition of the initiator, but under the conditions of saturation with oxygen they are rapidly transformed into the corresponding peroxy radicals ROO•. The rate of initiation, v_i, depends not only on the decomposition rate of the initiator but also on the activity of the R$^{\bullet}$ radicals and, hence, also on the cage effect of the medium. The propagation phase of the chain oxidation of lactams involves the reactions (*3*) and (*4*). Under the conditions of the reaction being independent of the oxygen pressure the oxidation rate is limited by the reaction step (*4*). This reaction produces the lactam hydroperoxide. The bimolecular termination leads to inert products: the cyclic imide and hydrogen peroxide[2]. The measure of oxidizability of lactam is the oxidizability parameter $k_p k_t^{-1/2}$ determined from the propagation rate

$$v_p = k_p k_t^{-1/2} [LH] v_i^{1/2}$$

and/or the kinetic length of the oxidation chains

$$\nu = v_p v_i^{-1} .$$

The oxidizability of lactams depends on their ring size[3]. In the oxidations carried out under the same conditions the reaction rates were distinctly different for the individual lactams. Pyrrolidone (L4) was oxidized with the kinetic chain length $\nu = 200$, whereas the corresponding values were 230 for piperidone (L5), only 12 for caprolactam (L6), 3 for enantholactam (L7), and 8 for capryllactam (L8). The differences in oxidizability of the lactams have no analogue in their other reactions, they are not connected with the conformation of amide group, the ring strain (in contrast to cycloparaffins whose oxidizability depends on the ring strain), and none of other usual physical properties of lactams[3]. Therefore we tried to find the explanation with the help of quantum-chemical methods.

CALCULATIONS

Beside the above-mentioned lactams L4 – L8 also studied were all their derivatives taking part in the oxidation process, i.e. the radicals L$^{\bullet}$, peroxy radicals LOO$^{\bullet}$, hydroperoxides LOOH, and cyclic imides. These molecules represent considerably extensive systems, and therefore we applied the semiempirical method[4] AM1 from the program set[5] AMPAC. This program was implemented on a computer class PC – LogoStar 386/33.

The calculations started from the models of fully optimized reactants. The starting lactam structures for the optimization procedure were taken from refs[6 – 9].

RESULTS AND DISCUSSION

Geometrical Structure of Lactams

The optimized geometries of the individual lactams calculated by the AM1 method are given in Table I. These values agree very well with results of analyses of the crystalline lactams[6 - 9]. The lactams L4 – L7 have a cisoid arrangement of the amide group, whereas in the lactam L8 the arrangement is transoid. The differences between the interatomic distances determined by the AM1 method and those measured for the lactams in solid phase did not exceed 0.05 Å in any case.

In comparison with the earlier calculations of the geometrical structures of lactams[10,11] carried out by the MNDO method[12], the AM1 method gives shorter bond lengths of all bonds except those of oxygen.

Energy Balance

The differences in oxidizability of lactams were interpreted by energy relations at first. Table II gives the energy changes accompanying the reactions (*3*) – (*5*).

In the initiation reaction (*2*) the only significant value is the relative difference of the dissociation energies of lactam into L$^{\bullet}$ and H$^{\bullet}$ radicals not involving the energy contributions of the simultaneous recombination of ROO$^{\bullet}$ and H$^{\bullet}$ which are independent of the lactam type.

The first step of the propagation phase of the oxidation, i.e. the reaction (*3*), is characterized by negative energy value ΔE_3. The differences between the individual ΔE_3 values were not distinct for the lactams studied, and they did not correlate with the oxidizability of the lactams (Table II). However, the reaction (*3*) is not the rate-limiting process[13] for the course of the chain oxidization independent of the oxygen pressure, hence this fact can be neglected.

The second propagation step, i.e. the reaction (*4*), can hypothetically be divided into two partial steps: the dissociation of lactam into the lactam radical and hydrogen atom

$$\mathrm{LH} \longrightarrow \mathrm{L}^{\bullet} + \mathrm{H}^{\bullet} \qquad (4a)$$

and the reaction of the lactam peroxy radical with hydrogen atom giving the lactam hydroperoxide

$$\mathrm{LOO}^{\bullet} + \mathrm{H}^{\bullet} \longrightarrow \mathrm{LOOH} \qquad (4b)$$

the first process being implicitly involved also in the initiation reaction (*2*). From Table II it can be seen that the ΔE_{4b} values are almost the same for all the lactams.

The energies of the termination reaction (*5*), ΔE_5, are relatively high (Table II), however, they show such a great scattering in the set of lactams studied that the interpre-

TABLE I
The optimized geometries of lactam molecules calculated by the AM1 method and the corresponding experimental values[a]

Atoms	Bond length, Å		Atoms	Bond angle, °		Atoms	Torsion angle, °	
	calculated	found[b]		calculated	found[b]		calculated	found[b]
				Pyrrolidone				
C2–C3	1.529	–	C2–C3–C4	105.4	–	C2–C3–C4–N	–1.3	–
C3–C4	1.547	–	C3–C4–N	107.1	–	C3–C4–N–C1	1.0	–
C4–N	1.443	1.455	C4–N–C1	112.5	114.9	C4–N–C1–O	179.7	–
N–C1	1.387	1.335	N–C1–O	124.3	125.8			
C1–O	1.240	1.232						
				Piperidone				
C1–C2	1.513	1.512	C3–C4–C5	110.9	109.6	C3–C4–C5–N	–43.4	–45.1
C3–C4	1.512	1.530	C4–C5–N	113.8	112.6	C4–C5–N–C1	15.6	13.3
C4–C5	1.529	1.521	C5–N–C1	124.8	126.4	C5–N–C1–O	178.9	177.7
C5–N	1.434	1.462	N–C1–O	119.0	122.0	C5–N–C1–C2	–2.0	–2.4
N–C1	1.378	1.333	N–C1–C2	119.8	117.9			
C1–O	1.249	1.243						
				Caprolactam				
C1–C2	1.514	1.513	C1–C2–C3	112.4	113.6	C4–C5–C6–N	–75.1	–77.0
C2–C3	1.514	1.535	C4–C5–C6	113.1	113.9	C5–C6–N–C1	63.6	67.8
C4–C5	1.511	1.539	C5–C6–N	116.4	113.7	C6–N–C1–O	176.5	176.6
C5–C6	1.528	1.525	C6–N–C1	125.6	125.5	C6–N–C1–C2	–3.7	–4.2
C6–N	1.431	1.480	N–C1–O	119.0	120.9	N–C1–C2–C3	–59.9	–63.1
N–C1	1.380	1.340	N–C1–C2	119.4	118.5			
C1–O	1.248	1.250						
				Enantholactam				
C1–C2	1.514	1.512	C1–C2–C3	111.2	111.4	C1–C2–C3–C4	–48.1	–48.9
C2–C3	1.514	1.538	C2–C3–C4	114.5	115.0	C5–C6–C7–N	78.3	73.1
C3–C4	1.516	1.533	C5–C6–C7	113.6	116.9	C6–C7–N–C1	–76.9	–81.7
C5–C6	1.514	1.535	C6–C7–N	116.2	113.9	C7–N–C1–O	173.4	181.2[c]
C6–C7	1.531	1.534	C7–N–C1	124.9	127.8	C7–N–C1–C2	–8.4	–1.4
C7–N	1.433	1.465	N–C1–O	118.1	120.0	N–C1–C2–C3	95.8	94.2
N–C1	1.384	1.337	N–C1–C2	121.1	119.9			
C1–O	1.249	1.249						
				Capryllactam				
C1–C2	1.518	1.510	C1–C2–C3	109.7	108.4	C1–C2–C3–C4	66.8	65.8
C2–C3	1.518	1.545	C2–C3–C4	115.0	115.1	C2–C3–C4–C5	–113.3	–109.2
C3–C4	1.518	1.545	C3–C4–C5	114.6	117.4	C6–C7–C8–N	58.3	58.3
C4–C5	1.515	1.527	C6–C7–C8	113.0	114.1	C7–C8–N–C1	–85.0	–90.5
C6–C7	1.517	1.547	C7–C8–N	114.6	109.4	C8–N–C1–C2	–40.7	–25.8
C7–C8	1.532	1.532	C8–N–C1	118.6	122.8	C8–N–C1–C2	140.0	148.4
C8–N	1.440	1.458	N–C1–O	121.4	122.4	N–C1–C2–C3	–87.1	–88.8
N–C1	1.390	1.342	N–C1–C2	117.7	115.0			
C1–O	1.244	1.242						

[a] The numbering of carbon atoms is the same as in the corresponding carboxylic acids, i.e. the carbonyl carbon atom is No. 1. [b] Refs [6–9]. [c] For the hydrochloride, ref[9].

tation of the lower oxidizability of higher lactams cannot be looked for in the preference of the termination to the propagation.

The decisive step of oxidation is the abstraction of hydrogen atom from the lactam molecule (reaction (*4a*)) and, in accordance with this fact, the energy differences ΔE_{4a} can be considered to be a criterion affecting the kinetic length of oxidation chains. The energies ΔE_{4a} of the lactams L5 – L7 correlate with the values $k_p k_t^{-1/2}$ (Table II). If this correlation is valid for the lactams L5 – L7, it must further be explained why the ΔE_{4a} values for the lactams L4 and L8 predict a distinctly slower oxidation as compared with experiment.

Hence the results of energy balances of the individual reaction steps of the oxidation mechanism mentioned do not completely explain the different reactivities of the lactams investigated.

Charge Distribution

There arises a question whether or not the oxidation reaction of lactams is controlled by the electrostatic situation in the molecule. Table III presents the electron density distribution at the atoms adjacent to the oxidation reaction centres. Except for the lactam radicals L$^\bullet$, all the systems show high values of partial electron charge at the nitrogen atom ($q_N \approx -0.4$ *e*), in most cases even higher than the charge value at the carbonyl oxygen atom. A similar result was obtained at the *ab initio* level with extended basis set[14]. In the L$^\bullet$ radicals the partial charge at nitrogen atom is lowered in favour of the carbon atom of methylene group adjacent to nitrogen where the unpaired electron is localized. Interestingly, the charge value of the hydrogen atom bound to this carbon atom remains almost unchanged when going from the radical L$^\bullet$ to the peroxy radical LOO$^\bullet$ ($q_H \approx -0.1$ *e*), although the charge magnitude of this carbon atom changes from $q_C \approx -0.2$ *e* to $q_C \approx -0.1$ *e*. However, the Mulliken analysis of the reactants did not show any dependence between the oxidizability and charge distribution – at least that obtained by the AM1 method (Table III).

TABLE II
Calculated energies (eV) of partial reactions and oxidizability parameters ($kg^{1/2}\ mol^{-1/2}\ s^{-1/2}$) of the lactams

Lactam	ΔE_3	ΔE_4	ΔE_{4a}	ΔE_{4b}	ΔE_5	$k_p k_t^{-1/2} . 10^3$
L4	-1.01	0.14	3.39	-3.25	-4.69	18.0
L5	-0.85	0.01	3.25	-3.25	-4.85	21.0
L6	-0.89	0.10	3.40	-3.30	-4.41	1.3
L7	-1.02	0.21	3.53	-3.32	-4.31	0.4
L8	-1.12	0.34	3.61	-3.27	-3.87	1.4

TABLE III

The values of partial charges (e) at the atoms in the vicinity of the reaction centre of oxidation of the lactams Ln (L4 – L8)

Atom	n = 4	n = 5	n = 6	n = 7	n = 8
			Lactam		
C(n)	−0.02	−0.01	−0.01	−0.02	−0.05
C(n − 1)	−0.17	−0.17	−0.18	−0.19	−0.19
N	−0.40	−0.39	−0.39	−0.38	−0.34
C1	0.31	0.31	0.30	0.30	0.29
O	−0.36	−0.38	−0.38	−0.38	−0.35
H(C(n))[a]	0.08	0.08	0.08	0.09	0.11
H(N)	0.25	0.23	0.23	0.23	0.19
			Lactam radical		
C(n)	−0.25	−0.24	−0.22	−0.19	−0.20
C(n − 1)	−0.11	−0.10	−0.10	−0.10	−0.13
N	−0.23	−0.21	−0.22	−0.27	−0.24
C1	0.25	0.25	0.26	0.28	0.27
O	−0.34	−0.36	−0.37	−0.36	−0.30
H(C(n))	0.17	0.15	0.14	0.12	0.16
H(N)	0.25	0.24	0.23	0.23	0.19
			Lactam peroxy radical		
C(n)	0.03	0.05	0.07	0.06	0.04
C(n − 1)	−0.17	−0.16	−0.18	−0.18	−0.19
N	−0.38	−0.37	−0.40	−0.40	−0.37
C1	0.30	0.30	0.32	0.32	0.30
O(C1)	−0.32	−0.34	−0.36	−0.36	−0.33
H(C(n))	0.14	0.13	0.11	0.12	0.16
H(N)	0.25	0.24	0.25	0.25	0.21
O(C(n))	0.07	0.05	0.09	0.09	0.09
O(O)	−0.23	−0.23	−0.22	−0.22	−0.21
			Lactam hydroperoxide		
C(n)	0.11	0.12	0.13	0.12	0.10
C(n − 1)	−0.17	−0.16	−0.18	−0.18	−0.18
N	−0.41	−0.39	−0.42	−0.41	−0.38
C1	0.30	0.30	0.32	0.31	0.30
O(C1)	−0.34	−0.36	−0.37	−0.38	−0.35
H(C(n))	0.13	0.12	0.11	0.12	0.12
H(N)	0.24	0.23	0.23	0.23	0.21
O(C(n))	−0.17	−0.18	−0.14	−0.15	−0.12
O(O)	−0.20	−0.20	−0.19	−0.19	−0.20
H(O)	0.20	0.20	0.20	0.20	0.23

[a] The values given represent an average value of the charges of both hydrogen atoms bound to C(n − 1).

Table IV gives the dipole moments calculated for all the species taking part in the oxidation reaction mechanism. The values found for the lactam molecules agree well with experimental data[15]. The dipole moments of the lactams and their radicals are practically independent of the lactam ring size. Certain differences can be seen in the dipole moments of peroxy radicals and hydroperoxides, but the differences between these values do not correlate with the oxidizability of the lactams investigated (Table II). The distinctly different value of dipole moment of capryllactam hydroperoxide is only due to the change in the geometrical structure (the transoid arrangement), which is shown by both the distribution of individual charges (Table III) and the fact that the dipole moment of cisoid conformation of capryllactam hydroperoxide is equal to 2.4 D.

Frontier Orbital Interactions

We also tried to explain the different oxidizability of lactams on the basis of the theory of frontier orbitals[16]. The distribution of energy values of molecular orbitals in the HOMO-LUMO region can be used for the estimation of relative rates of various bimolecular reactions.

In the reaction (*3*), the LUMO of oxygen interacts with the SOMO of L$^{\bullet}$. The quantity Δe_3 represents the energy difference between the LUMO of oxygen molecule and the SOMO of L$^{\bullet}$ radical (Table V). The AM1 program does not give completely correct energy values of the HOMO and LUMO of O_2 molecule (–10.49 and –0.52 eV), because it does not take into account the degeneration of the partially occupied orbitals π_y and π_z which causes the paramagnetic behaviour of oxygen. Nevertheless, since the relative differences Δe_3 (Table V) between the individual systems only depend on the SOMO energy of the radical, the mentioned inaccuracy will not make itself felt.

The reaction (*4*) is the rate-limiting process of the chain oxidations independent of the oxygen pressure[13]. In this reaction the HOMO of lactam interacts with the SOMO of peroxy radical. The energy differences of the two orbitals, however, give no unambi-

TABLE IV
The calculated dipole moments (D) of lactams and related species

Species	L4	L5	L6	L7	L8
Lactam[a]	3.8	4.0	4.0	3.8	3.6
	(3.6)	(3.8)	(3.9)	(3.9)	(3.9)
Lactam radical	3.1	3.3	3.2	3.2	3.9
Lactam peroxy radical	3.4	4.2	4.5	4.5	5.1
Lactam hydroperoxide	1.9	2.4	2.5	2.5	4.8

[a] Experimental values[15] are in parentheses.

guous statement about different oxidizability of lactams. The higher values Δe_4 – as compared with Δe_3 (Table V) – and hence the weaker mutual interaction of energy levels are in accordance with the fact[13,17] that the rate of step (*3*) is considerably higher than that of the reaction (*4*) under the conditions given.

The termination (*5*) is a bimolecular reaction of two identical particles LOO$^\bullet$ involving an interaction of two SOMO's, hence it is irrelevant to speak about the energy differences Δe_5.

Plane of Symmetry

The interpretation of different oxidizability of the lactams L4 and L8 in the chain oxidation as compared with the lactams L5 – L7 can be given in two steps – with the help of energy criteria and by further analysis of the eigenvectors of the systems studied. The transition of the lactams L4 – L7 to the respective radicals L$^\bullet$ involves a crossing of the molecular orbitals of the electron pair at nitrogen with those of the electron pair at oxygen (Fig. 1). Only in the case of capryllactam (L8), the energy order of MO's of the given electron pairs remains unchanged. Therefore, the crossing of MO's should result in an almost zero reactivity in the case of the lactams L4 – L7, because the reactions are symmetry-forbidden[18]. However, this reaction step is

TABLE V
The energies of frontier orbitals (eV) of lactams LH, lactam radicals L$^\bullet$, lactam peroxy radicals LOO$^\bullet$, and the energy differences of the interacting orbitals (Δe, eV) in the reactions (*3*) and (*4*)

System	$e_{HOMO}(LH)$ $e_{LUMO}(LH)$	$e_{HDOMO}(L^\bullet)$ [a] $e_{LUMO}(L^\bullet)$	$e_{SOMO}(L^\bullet)$ $e_{SOMO}(LOO^\bullet)$	Δe_3 [b,c]	Δe_4 [d]
L4	−9.93	−10.92	−3.63	3.11	4.26
	1.53	1.41	−5.67		
L5	−9.85	−10.74	−3.62	3.10	4.32
	1.56	1.48	−5.51		
L6	−9.90	−10.82	−3.74	3.22	4.11
	1.56	1.44	−5.76		
L7	−9.89	−10.47	−4.05	3.53	4.24
	1.51	1.39	−5.65		
L8	−9.50	−10.54	−3.87	3.35	4.13
	1.43	0.99	−5.37		

[a] HDOMO the highest double occupied MO; [b] $\Delta e_3 = e_{LUMO}(O_2) - e_{SOMO}(L^\bullet)$; [c] $e_{LUMO}(O_2) = -0.52$ eV; [d] $\Delta e_4 = e_{SOMO}(LOO^\bullet) - e_{HOMO}(LH)$.

probably only slowed down, because in this case radical particles are formed for which violations of symmetry rules are not quite exceptional (due – first of all – to a higher spin–orbital interaction).

The fully optimized model of pyrrolidone molecule shows its membership of the point group of symmetry C_S with planar arrangement and a plane of symmetry σ (see the values of torsion angles in Table I). It has turned out that the MO of the nitrogen electron pair is orthogonal to the symmetry plane σ and belongs to the representation A″, whereas the MO of oxygen electron pair lies in the plane of symmetry and belongs to the representation A′. This means that the dissociation of pyrrolidone according to

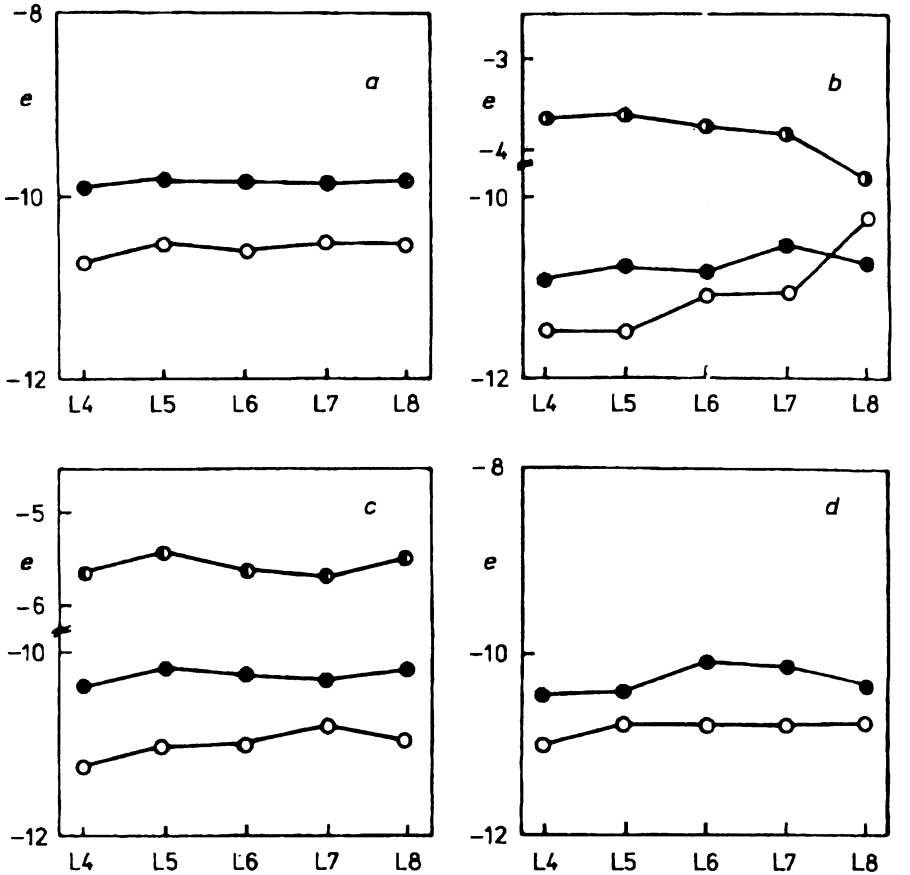

FIG. 1

The dependences of the MO energies (eV) on the ring size for the lactams LH (*a*), lactam radicals L$^{\bullet}$ (*b*), lactam peroxy radicals LOO$^{\bullet}$ (*c*), and hydroperoxides LOOH (*d*). MO localized on: ○ carbonyl oxygen, ● nitrogen, ◐ oxygen radical, ◑ carbon (C(*n*)) radical

Eq. (*4a*) is not connected with a symmetry-forbidden crossing of orbitals and thus the abstraction of hydrogen belongs among the allowed reactions. A different situation is encountered with the lactams L5 – L7 whose molecules belong to the point group of symmetry C_1 so that the dissociation mentioned is forbidden for them.

Hence, the oxidation rates of pyrrolidone and capryllactam are not affected by the symmetry rules, whereas those of piperidone, caprolactam, and enantholactam are lowered.

CONCLUSION

The oxidizability $k_p k_t^{-1/2}$ found experimentally for lactams exhibits a dependence on the ring size. For the reactions independent of the oxygen pressure the rate-limiting process is the abstraction of hydrogen from the lactam molecule to give the respective radical. This reaction is involved in both the initiation and propagation steps of the chain mechanism. For the lactams L4 – L8 the energy changes belonging to this reaction were calculated by the AM1 method. The correlation of their values with the values of oxidizability parameters was obvious only after the analysis of symmetries of molecular orbitals.

Except for capryllactam, all the lactams exhibit a crossing of the MO's of the electron pair at nitrogen and that at oxygen during their transformation into the corresponding radicals. As the structures of piperidone, caprolactam, and enantholactam belong to the point group of symmetry C_1, the dissociation mentioned is symmetry-forbidden for these lactams. Pyrrolidone belongs by its geometry to the point group of symmetry C_S, hence the symmetry-forbidden crossing of the corresponding MO's is not encountered here. Thus for pyrrolidone and capryllactam the oxidizability parameter can be directly correlated with the corresponding dissociation energy ΔE_{4a}, whereas for piperidone, caprolactam, and enantholactam we must take into account a retardation of the reaction caused by the symmetry-forbidden crossing of the MO's of the free electron pairs at nitrogen and oxygen.

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