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Polymer Degradation and Stability 74 (2001) 569–577

Polymer Degradation and Stability

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An ab initio quantum chemical study of reactions of hexano-6-lactam peroxy radicals with phenoxy or diphenyl radicals

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Received 7 April 2001; received in revised form 21 June 2001; accepted 27 June 2001

Abstract

Molecular mechanism of the inhibition reaction of lactam peroxy radicals with phenoxy and diphenylaminyl radicals yielding cyclic imide was studied. Ab initio quantum chemical methods—MP2 and DFT were used for models where benzene rings were replaced with methyl groups to find the transition state between the complex of starting radicals and the complex of products. Both methods give qualitatively similar results. For calculations of real systems with phenyl substituents, only DFT method was used. A transition state was found for the reaction of both types of radicals. The reaction can occur through a four-membered ring in the reaction center, breaking the O–O bond of the lactam peroxy radical HCOO$^{\bullet}$ with simultaneous transfer of hydrogen from the carbon atom to the departing oxygen. The $^{\bullet}$OH formed combines with the phenoxy or diphenylaminyl radical. The activation barriers for the suggested inhibition are very low (less than 30 kcal mol^{-1}). Final gains of energy for the reaction were found to be about 70 kcal mol^{-1} for diphenylaminyl radical and about 50 kcal mol^{-1} for phenoxy radical. Thus, both reactions should be exothermic.

Keywords: Ab initio calculations; Lactams; Reaction mechanism; Transition state

1. Introduction

While studying the efficiency of stabilizers in oxidation of lactam-based polyamides, we have followed the kinetics and mechanism of the oxidation of hexano-6-lactam in the presence of antioxidants, derivatives of phenol and diphenylamine [1,2]. We have proved that the first inhibition reaction of hexano-6-lactam peroxy radical with these compounds leads to hexano-6-lactam hydroperoxide and a phenoxy or aminyl radical of the antioxidants. Further inhibition reaction of these radicals, i.e. reaction of a diphenylaminyl or phenoxy radical, with lactam peroxyl, has an oxidation–reduction character and leads to inactive molecules. By reduction of the peroxyl, an imide is formed (adipimide in the case of hexano-6-lactam). Aminyl radicals are oxidized to derivatives of *N*,*N*-diphenylhydroxylamine [3–8]. Dimers or even higher associates of hydroxycyclohexa-2,5-dien-1-one derivatives are hypothetical products of phenoxy radicals [9–11]. While the derivatives of *N*,*N*-diphenylhydroxylamine react with peroxyls and thus inhibit further oxidation chains, the inhibiting ability of phenol-based radicals is exhausted. In oxidations of *N*-alkylamides, one molecule of a secondary aromatic amine antioxidant can interrupt ten oxidation chains [2], whereas one molecule of phenol derivatives interrupts only two [2,11].

Hydroxylamine derivatives have been found in the products of secondary aromatic amine radicals with peroxy radicals, whereas possible products of phenol radicals are only a topic of hypotheses [3–11]. The molecular mechanism of the reactions of *N*-alkylamide peroxy radicals and oxy or aminyl radicals has not been safely determined [12–19]. Undoubtedly this mechanism will be similar to the termination reaction of peroxy radicals of *N*-alkylamides, which is bimolecular, yielding two molecules of imide and one molecule of hydrogen peroxide [20]. A similar termination of peroxy radicals is assumed by Lee and Mendenhall [21] in oxidations of hydrocarbons. They postulate a mechanism where a tetroxide intermediate is formed first, and then gradually decomposed by two consecutive reactions

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0141-3910/01/$ - see front matter
PII: S0141-3910(01)00194-X

through a trioxide intermediate to final products: two molecules of ketone and one molecule of hydrogen peroxide [21].

We have attempted to elucidate the course of the reaction of hexano-6-lactam peroxy radicals with phenoxy or diphenylaminyl radicals using the tools of quantum chemistry.

2. Computational details

In the study of the reaction of peroxy radicals of hexano-6-lactam with oxy or aminyl radicals of phenolic and secondary aromatic amine derivatives, the corresponding radicals were modelled by their methyl analogues, i.e. phenoxy radical by methoxy, and diphenylaminyl by dimethylaminyl radical. Thus, we arrive at the following reactions of Schemes 1 and 2.

The reason for this substitution consists in a substantial reduction of the electron number in the studied system. For such reduced models of inhibition reactions, it was possible to compare two different methods—MP2 and DFT. While the perturbation theory method in our case with frozen core [MP2(FC)] is based on the wave function formalism, density functional method (DFT) uses for the description of the studied systems electron density. In this study the Becke's three-parameter hybrid exchange-correlation functional [22,23] was chosen:

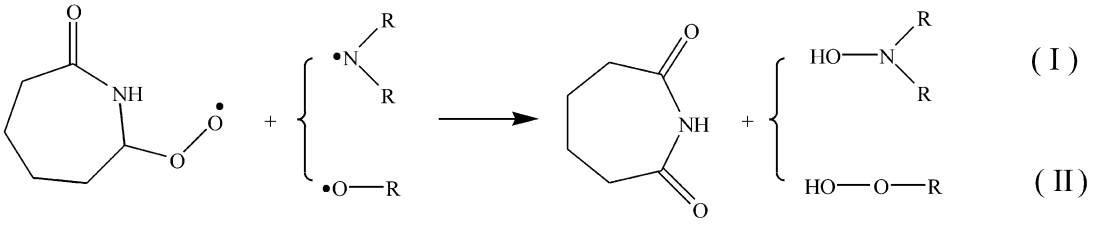
$$E = A.E_X^{\text{Slater}} + (1-A).E_X^{\text{HF}} + B.E_X^{\text{Becke}} + (1-C).E_C^{\text{VWN}} + C.E_C^{\text{LYP}}.$$

Here E_C^{VWN} is the local correlation term, and E_C^{LYP} is a combination of both local and non-local correlation functional. Standard 6-31G* basis set [24] was used in both methods (MP2(FC)/6-31G* and B3LYP/6-31G*). In this way, it can be estimated how much the DFT (B3LYP) method deviates for the determination of "long-term" dispersion energy contributions [25, 26] which are present in the two-species interaction (in our case mainly in the transition state and product complexes). Initial radical particles were treated within unrestricted formalism, all the other reaction species were computed in restricted framework. All the calculations were performed with the standard quantum chemical program packet Gaussian 94.

The initial radicals (reactants) and resulting molecules (products) of the Schemes I and II were at first optimized as isolated species. Several conformers of the lactam ring were compared and the energetically lowest one was further used. The geometry of this conformer is in very good agreement with the experimentally observed structure [27,28]. Then the other two optimizations of the complexes of reactants and products as closed-shell pseudo-molecules were performed. In this manner, two additional steps can be defined: an associative step, when initial radicals come from infinity (isolated species) and form the complex of reactants (for the optimized structure see Fig. 1a), and a dissociative step when the H-bonded product complex (Fig. 1c) is broken. Also in these cases several mutual orientations were explored. Despite the existence of many local minima, we hope that all the most important ones were searched; the energetically deepest ones are presented in the Fig. 1.

For the associative and dissociative steps, the BSSE counterpoise error [29] and the deformation energy corrections were determined. Deformation energy is defined as the energy difference between the optimized isolated species and its structure taken from the optimized complex [30].

As the last step of our work, structure of the transition state (TS) between reactants and products was searched for (cf. Fig. 1b). These structures were usually successfully estimated so that the proper imaginary eigenvalue of the Hessian matrix was found (using analytical second derivatives calculations) and relatively easily followed. However, in the reaction of the dimethylaminyl radical, using the MP2 method, the correct structure was revealed only by the treatment of quadratic synchronous transit algorithm [31,32] (QST3). This method is designed so that the transition-state structure is estimated not only from our ‚chemical intuition" but partially also from desired reactants and products.



R = methyl or phenyl

Schemes I and II.

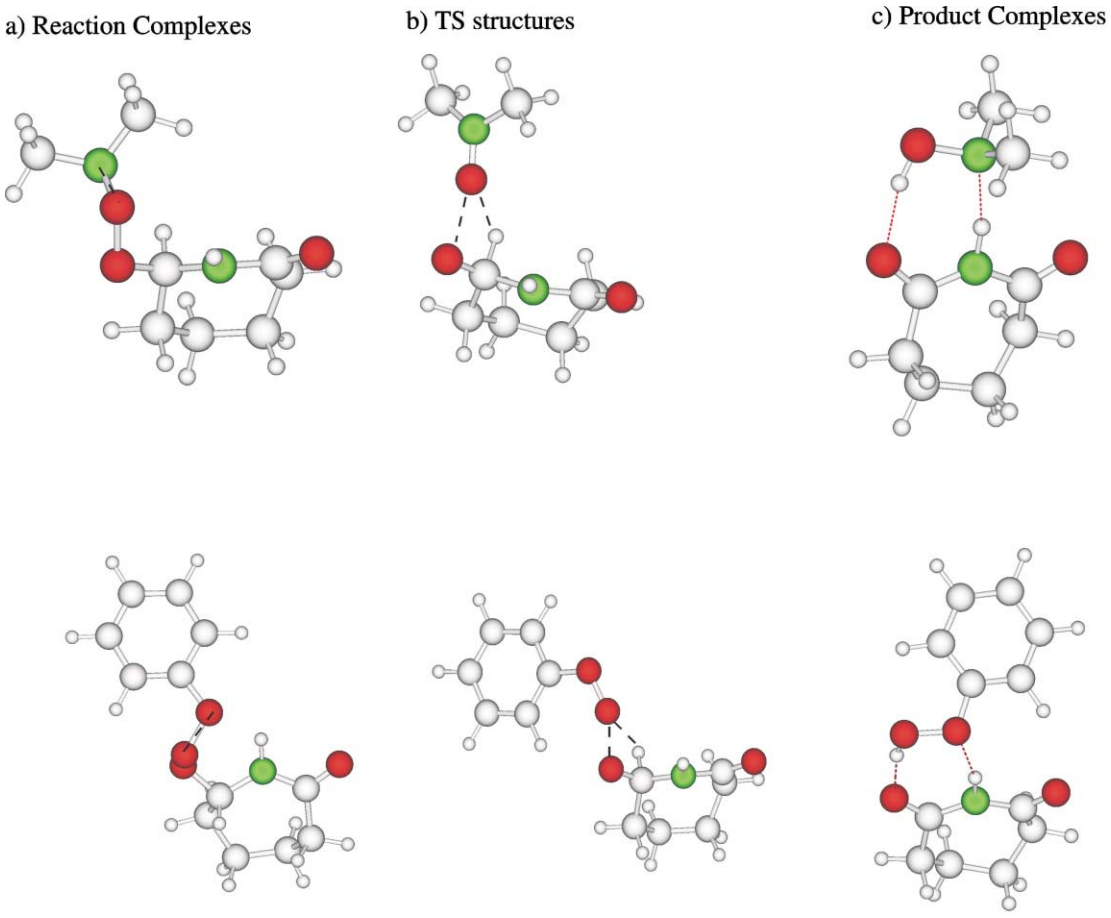


Fig. 1. The optimized structures of hexano-6-lactam peroxy radical with dimethylaminyl radical and phenoxy radical (DFT method) in: (a) reactant complex; (b) TS structure; (c) product complex. The oxygen and nitrogen atoms are shaded.

Moreover standard algorithm requires one negative eigenvalue of hessian matrix in order to follow the corresponding eigenvector uphill. This requirement is not crutial (al least at the beginning) in QST3 algorithm which is very important in cases with more complicated energy surface. However, the detailed analysis of the standard-method failure in the MP2 case was not done.

With the knowledge of the energy surface of the methyl analogues, the reactions of hexano-6-lactam peroxy radical with diphenylaminyl or phenoxy radical were explored. For such a large model, only the DFT method was used.

In the whole study, the atoms at interaction sites of the reactants were designated according to the scheme in Fig. 2: in (a) hexano-6-lactam peroxy radical, (b) dimethyl or diphenylaminyl radical, and (c) methoxy or phenoxy radical. The numbering of atoms is preserved in the course of the reaction.

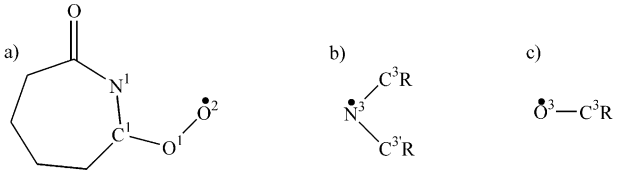


Fig. 2. Schematic picture of the atomic labels of interacting radicals.

3. Results and discussion

3.1. Geometry parameters

3.1.1. Starting radicals

Complexes of hexano-6-lactam peroxy radical with aminyl or phenoxy radicals (reactant complexes) were created. Since in the studied inhibition reactions both starting species are radicals, the recombination of their single electrons results in the formation of a covalent bond and leads to a closed-shell molecule (Fig. 1a). Despite the relatively strong associative interaction, no remarkable changes in the geometry of the hexano-6-lactam ring in these complexes were observed. The only exception was the complex of the lactam peroxy radical with the diphenylaminyl radical (Scheme I, R = phenyl) where some deformation of the lactam ring is apparent. Also some small reorientation of benzene rings relative

to the amine nitrogen as compared with the isolated diphenylaminyl radical, was observed.

A detailed view of structural parameters is shown in the first part of Table 1 (reactant complexes) where the most important bond lengths and angles in the reaction centers of the reactant complexes are collected.

Comparing the optimized geometries obtained by both the MP2 and DFT methods, very similar structures are obtained for the complexes of hexano-6-lactam peroxy radical both with dimethylaminyl (Scheme I) and with methoxy (Scheme II) radicals. Marginal deviations can be observed only in the region of bridges O^1–O^2–N^3 (Scheme I; for labeling of atoms, see Fig. 2) and O^1–O^2–O^3 (Scheme II). This fairly good agreement between the results of the MP2 and DFT methods is associated with the fact that a covalent bond is formed when the two radicals interact.

In comparing the results for methyl- and phenyl-substituted radicals obtained by the DFT method some differences can be seen. This is, however, not surprising because the interaction benzene ring...lactam is of different character than the interaction methyl...lactam, and thus somewhat different torsion angles are expected. From the first part of Table 1 (reactant complexes), it can be seen that the character of the C^1–O^1–O^2–N^3 bridge of the diphenylaminyl radical with lactam peroxy radical complex is different from all the others. Probably, under the steric influence of the two benzene rings of the diphenylaminyl radical, the lactam ring is in this complex a little pushed off from the N^3–O^2 atoms. This leads to the lengthening of the bridge O^1–O^2 bond and enhanced double bond character of the other bonds, e.g. N^3=O^2 and C^1=O^1. Such a "deconjugation" was not observed in the case of phenoxy radicals (Scheme II). There is only one phenyl group here, and hence this species behaves similarly to the methyl-substituted model.

3.1.2. Transition states

A very interesting part of this study lies in the determination of the TS structures. These structures are based on a four-membered ring ..O^2..H–C^1–O^1.. where the outer oxygen O^2 from the lactam peroxy group (now partially broken) interacts simultaneously with hydrogen H(C^1) and the previously bonded oxygen O^1 (Fig. 1b)—syn-elimination. This situation reflects the fact that the central bond O^1–O^2 of the N^3–O^2–O^1–C^1

Table 1
Atom distances (Å), bond and torsion angles (°) at the interaction sites in reactions of lactam peroxy radical with the dimethylaminyl (I), diphenylaminyl (I′), methoxy (II) and phenoxy (II′) radicals (Schemes I and II) as calculated by MP2 and DFT methods

Geometry param.	I (MP2)	I (DFT)	I′ (DFT)	II (MP2)	II (DFT)	II′ (DFT)
(a) Reactant complexes						
C^1–O^1	1.419	1.413	1.378	1.427	1.426	1.503
O^1–O^2	1.484	1.480	1.758	1.465	1.452	1.457
O^2–X^3 [a]	1.429	1.414	1.287	1.440	1.427	1.477
N^1–C^1–O^1	108.1	108.5	109.2	107.9	108.2	107.3
C^1–O^1–O^2	107.6	109.3	105.3	107.5	108.9	106.1
O^1–O^2–X^3 [a]	106.5	108.0	108.8	106.4	107.8	105.9
C^1–O^1–O^2–X^3 [a]	70.4	72.7	155.3	77.3	79.6	−84.6
(b) TS structures						
C^1–O^1	1.374	1.296	1.299	1.332	1.304	1.306
O^1...O^2	2.464	2.265	2.350	2.381	2.041	2.067
O^2–X^3 [a]	1.357	1.264	1.273	1.340	1.344	1.347
O^2...H(C^1)	2.115	1.682	1.708	1.646	1.612	1.648
H(C^1)–C^1	1.101	1.188	1.181	1.157	1.200	1.188
X^3–O^2...H(C^1) [a]	164.1	146.6	142.0	139.6	150.1	150.6
O^2...O^1–C^1	76.7	81.1	81.0	77.7	84.6	84.3
O^1...O^2–X^3 [a]	138.5	155.1	151.4	164.9	147.1	147.2
C1–O^1...O^2–X^3 [a]	−136.6	−162.4	−135.6	−179.2	−173.2	−177.2
(c) Product complexes						
C^1–O^1	1.240	1.232	1.232	1.238	1.231	1.232
O^1...H(C^1)	1.917	1.875	1.811	1.890	1.847	1.803
H(C^1)–O^2	0.986	0.984	0.987	0.989	0.988	0.991
O^2–X^3 [a]	1.445	1.437	1.429	1.473	1.459	1.448
X^3...H(N^1) [a]	1.809	1.841	1.999	1.874	1.884	1.980
N^1–H	1.051	1.050	1.035	1.032	1.031	1.026
N^1–H...X^3 [a]	170.2	169.7	166.6	168.5	168.2	164.5
O^1...H–O^2	165.1	166.0	169.8	168.3	169.1	169.2
O^1...O^2–X^3 [a]	91.6	92.9	97.0	91.5	91.9	92.8
C^1–O^1–O^2–X^3 [a]	−11.7	−8.1	−8.8	−28.4	−17.9	8.6

[a] X=N (reactions with I and I′) or O (reactions with II and II′).

(Scheme I) or of O^3–O^2–O^1–C^1 (Scheme II) in the reactant complexes is very weak and can be easily broken.

Geometric parameters of these TS structures (Table 1, part TS) calculated by the MP2 and DFT methods are again in fairly good agreement. The only exception is the transition state of the reaction of lactam peroxy radical with dimethylaminyl radical. At the MP2 level of theory, the O^2...H(C^1) bridge is relatively longer (about 2.1 Å) and, also, the C^1–O^1 bond length resembles more or less a single bond length (Table 1). A similar central part of the TS structures of oxy radical reactions (Scheme II) is predicted consistently using both methods.

3.1.3. Reaction products

The studied inhibition reactions lead to adipimide as a product of the reduction of hexano-6-lactam peroxy radical. By oxidation of radicals, hydroxylamine derivatives are formed with secondary aromatic amines and phenyl hydroperoxide derivatives with phenols. The complex of adipimide with the radical products (product complexes) is stabilized by two H-bridges forming a slightly deformed seven-membered ring (Fig. 1c). Since these H-bonds cause a weak perturbation (about 10–16 kcal mol^{-1}), the geometry deformations of the radical products in these complexes are negligible as compared with isolated molecules. Some important geometry parameters of product complexes are compiled in Table 1 (Product complexes). It can be seen here that no substantial differences between the geometries obtained with MP2 and DFT occurred in the case of weakly interacting species in product complexes.

In contrast to components in reactant complexes, mutual orientation of the lactam ring and aminyl or oxy radical is better preserved even in phenyl-substituted systems (Schemes I and II for R = phenyl). Only the seven-membered lactam ring itself deviates in the diphenylaminyl reaction (Scheme I) from the others and the (N^1)H...N^3 H-bond is slightly longer as compared with the product complex of reaction with phenoxy radical.

The hydroperoxy group –C^3–O^3–O^2–H in benzene hydroperoxide molecule is coordinated in the plane of the benzene ring in the same way as the skeleton of the styrene molecule.

3.2. Energetics

The whole inhibition reaction of lactam peroxy radical with phenoxy or aminyl radical of phenol or diphenylamine derivatives, can be separated into several consecutive steps: association of radicals, TS formation, product formation and product dissociation. In Table 2, reaction energies of all these steps together with the total energy balance for reactions from Schemes I and II are summarized.

The first step is associated (as stated above) with the creation of a covalent bond from single electrons localized in SOMO of both reactant species. The association of reactants, producing the reactant complex (Fig. 1a) is accompanied by an energy release of about 43 kcal mol^{-1} after BSSE corrections in the case of the dimethylaminyl radical interaction (Scheme I) at the MP2 level (Table 2). In the case of methoxy radical (Scheme II), the amount of released energy is a little smaller (about 31 kcal mol^{-1} at the same theory level). These energy estimations decrease when the DFT method is used (34 and 24 kcal mol^{-1}, respectively). Passing from methyl-substituted to phenyl-substituted model radicals, the association energy is further decreased. This means that the O^1–O^2 bridge is weakened. This is in accord with the fact that this bridge is longer in the case of phenyl species (Schemes I and II, R = phenyl). Here, an agreement with chemical understanding of the role of individual substituents is demonstrated. Methyl is considered as a donor of electron density on the contrary to phenyl ligand. Thus, electron density over O^1–O^2 is larger and slightly stronger bond is formated in the case of methyl substituents.

There is virtually no energy gain in the analogous associative interaction of phenoxy radical (Scheme II). A possible explanation can be seen in Coulomb interactions. Despite of the larger dipole moment with the isolated phenoxy radical as compared to the isolated methoxy radical, the dipole moment for the reactant complex in the Scheme II for phenyl substituent is lower in comparison with a similar complex with methyl substituent (cf. Table 3). This inconvenient mutual orientation of the dipole moments of both lactam peroxy radical and phenoxy radical in the reactant complex may be another reason for the energetic instability of the O^1–O^2–O^3 chain.

When the deformation energies are compared, an interesting picture is obtained (cf. Table 4). While negligible values can be seen for product complexes, deformation energies for reactant complexes are remarkably higher. The explanation consists in the fact that molecules in product complexes are only very weakly bonded (slightly more than 10 kcal mol^{-1}) but in reactant complexes radicals are firmly connected with covalent bond. Such an interaction can deform the original structures to the large extent. In the case of methyl-substituents only changes on lactam rings are visible; small dimethylaminyl- and/or methyloxy-radicals are sufficiently flexible. On the contrary, the large diphenylaminyl radical is influenced substantially, especially the mutual orientation of both phenyl rings. That is why the phenoxy radical does not exhibit similar behavior. Deformation energy of the diphenylaminyl radical is 37 kcal mol^{-1}. In the case of the phenoxy radical, it is only 6 kcal mol^{-1}.

The following step—formation of the TS (Fig. 1b)—is an endothermic process (Table 2). Nevertheless, the

energy barriers are very low. In the reaction of the dimethylaminyl radical, the barrier is even covered by the energy gain from the association process (Table 2). The extremely low activation barrier in the MP2 description of this system (about 6 kcal mol^{-1}) reflects the small difference between the geometry of the reactant complex and the geometry of TS, i.e. similar $O^2...H(C^1)$ and $C^1–H(C^1)$ distances. In this case, the very small value of the TS dipole moment ($\mu = 2.3$ D) is also quite striking (cf. Table 3). This fact is associated with partial charge distribution and it is discussed below.

In the case of methoxy and phenoxy radicals, the energy barriers for reactions (Scheme II) are a little higher and, according to DFT predictions, the energy gain from association does not cover them completely (Table 2). This is, however, of small importance since the barrier is also relatively very low and the total reaction process is sufficiently exothermic.

The next step—creation of the complex of products—is associated with the energy release of about 70 kcal mol^{-1} (Table 2) in the case of aminyl radicals (Scheme I) and about 90 kcal mol^{-1} for oxo radicals (Scheme II). In contrast to the association energies, the predicted energies for the formation of TS and energies released within the creation of the complexes of products are larger using the DFT method. These values are also very similar for both methyl- and phenyl-substituted systems.

The TS is virtually the only structure where at least some difference between MP2 and DFT description can be seen. Comparing both approaches, formation and decomposition energies differ by about 5–9 kcal mol^{-1}. Such a difference is still within the computation error but because of more or less systematic treatment of these systems, we believe the correct energy should be closer to MP2 values, the DFT energies overestimating the true energy barriers in this case. Nevertheless, we are aware that it is not possible to uncritically rely on the 2nd order of perturbation theory and other calculations at higher level of theory would be necessary to make the picture entirely clear.

The last step—dissociation of the product complexes (Fig. 1c)–involves breaking of two H-bonds, which is energetically not too demanding. For all reactions, (Schemes I and II), the energies are fairly similar (Table 2). Nevertheless, it is interesting to note that the product complexes of reactions from the Scheme I are a little more stable, probably due to higher partial charge on O^2 in the amine–oxide complex than in the peroxide complexes of the Scheme II.

Table 2
Energies (in kcal mol^{-1}) of reaction steps in the reaction of hexano_6_lactam peroxy radical with aminyl radicals (I for methyl and I' for phenyl substituents) and oxy radicals (II for methyl and II' for phenyl substituents)

Step[a]	I (MP2)	I (DFT)	I′ (DFT)	II (MP2)	II (DFT)	II′ (DFT)
RA	−52.87	−38.44	−26.13	−37.87	−27.52	−2.92
BRA	−42.93	−33.66	−20.62	−30.92	−23.87	2.06
FTS	5.81	14.26	13.54	23.56	31.88	28.91
CP	−74.26	−79.88	−72.16	−86.80	−91.65	−89.18
DP	16.60	14.37	13.42	14.13	12.67	11.45
BDP	11.72	11.07	9.05	9.54	9.37	7.73
TR	−104.73	−89.69	−71.33	−86.98	−74.62	−51.75

[a] RA—radical association (reactant complex), BRA—BSSE corrected radical association, FTS—formation of TS, CP- creation of the product complex, DP—dissociation of the product complex, BDP—BSSE corrected dissociation of the product complex, TR—total reaction.

Table 3
Dipole moments μ (D) of species in the reaction of hexano-6-lactam peroxy radical (LOO•) with aminyl radicals R_2N• (I–R = methyl, I′-R = phenyl) and oxy radicals RO•(II–R = methyl, II′–R = phenyl)

Reaction (method)	I (MP2)	I (DFT)	I' (DFT)	II (MP2)	II (DFT)	II' (DFT)
Reactant complex	4.24	4.45	6.40	5.14	5.14	3.75
TS structure	2.38	7.71	7.67	6.23	5.54	5.86
Product complex	3.54	3.75	4.95	5.00	5.05	5.88
R_2N•/RO•	1.85	1.76	1.52	1.99	2.01	3.67
R_2NOH/ ROOH	0.73	0.77	1.21	1.65	1.74	1.60
Adipimide	4.63	3.85	3.85			
LOO•	4.54	4.50	4.50			

Table 4
Deformation energies (in kcal mol^{-1}) of species R_2N• and LOO• in reactant complex and R_2NOH and adipimide in product complex in the reaction of hexano-6-lactam peroxy radical (LOO•) with aminyl radicals R_2N• (I - R = methyl, I′- R = phenyl) and oxy radicals RO• (II - R = methyl, II' - R = phenyl)

	I (MP2)	I (DFT)	I′ (DFT)		II (MP2)	II (DFT)	II′ (DFT)
Reactant complexes							
R_2N•	0.8	1.0	5.6	RO•	0.8	0.0	9.9
LOO•	10.7	9.0	36.9	LOO•	8.0	6.4	5.8
Product complexes							
R_2NOH	0.6	0.4	0.5	ROOH	0.3	0.1	0.2
Adipimide	0.3	0.2	0.7	Adipimide	0.3	0.3	0.5

The total energy of the explored reactions according to Schemes I and II is defined as difference of isolated product molecules and isolated radical species. The MP2 value for the system containing dimethylaminyl radical is about 105 kcal mol^{-1} and about 87 kcal mol^{-1} for the methoxy radical system (Table 2). These values are about 10 kcal mol^{-1} higher than those obtained with the B3LYP functional. The total energies for phenyl-substituted reactions are lower by about 20 kcal mol^{-1}. This is caused not only by steric effects (observed in the case of diphenylaminyl radical, Scheme I) but predominantly by changed electron density in the reaction centers.

Both the complexes of reactants and products were also reoptimized in triplet states. However, energies of such complexes in triplet states remain higher than the corresponding values of the singlet states structures. The complexes of reactants in triplet states were substantially closer to singlets (about 6 kcal mol^{-1}) for both aminyl- and oxy-radicals. Here one could observe also some distinct prolongation of O^1-O^2 bonds. However it seems that the single-determinant method is not suitable for the description of the systems since some bond-breaking (O^1–O^2) already happened, stabilizing not complex of reactants but some intermediates.

3.3. Electron density analyses

Mulliken population analyses were performed for all studied systems (Schemes I and II). In the case of MP2 method, additional natural bond analysis [33] (NBO) was done. Partial charges for some atoms of the reaction centers C^1, O^1, O^2, $X^3 = N^3/O^3$, and C^3 are summarized in Table 5. Comparing all three parts of the table, several apparent trends can be noted.

The most striking general trend remarkable in all three reaction states (reactant complexes, TS structures, and product complexes) concerns the qualitative difference of partial charges on carbon atoms adjacent to the nitrogen of aminyl radical and to the oxygen of oxy radical when passing from the methyl- to phenyl-substituted systems. This has consequences in smaller reaction and association energies of both phenyl-substituted systems (Table 2).

In the reactant complexes (Table 5, part a), it can be seen that for the reactions of aminyl radicals (both methyl- and phenyl-substituted), electron density is more or less evenly distributed over the O^1–O^2–N^3 bridge. On the contrary, for the oxy radical systems (Scheme II) there is a remarkable decrease in electron density on the middle oxygen O^2 of the O^1-O^2-O^3 bridge. The lower electron density correlates with the smaller association energies of oxy radicals compared with aminyl radicals (Table 2). Probably some general consequences about low stability of –O–O–O– chains can be drawn.

Passing from methyl to phenyl substituted systems, another important feature can be observed. Namely, an increase of the negative partial charge on the X^3 atom. On the assumption that this X^3 atom is connected in the association step with another negatively charged atom (O^2), it is clear why such an association is less feasible in phenyl-substituted systems.

Interesting dependences can be observed for partial charges of TS structures. Focusing on aminyl systems (Scheme I), the following relation appeared. The partial charge on the N^3 atom of dimethylaminyl species is substantially reduced using both the MP2 and DFT methods (Table 5, part b) in comparison with those in reactant and product complexes. Such a reduction is not so pronounced for the diphenylaminyl radical where a value similar to that in reactant and product complexes is preserved in the TS structure as well. It is also not surprising that the partial charge on the oxygen O^2, already linked in the TS structure to the amine N^3, resembles the corresponding value in the product complex. In this manner, the binding relations in this part of structure start being similar to the product state. It is also interesting that in the MP2 description, the partial charge on the oxygen O^1 from lactam peroxy group is temporarily reduced in TS, while the DFT results leave this value similar to that in the reactant complex. This difference in the charges using the MP2 and DFT methods corresponds to a similar difference in the geometries of TS structures predicted by the two methods (cf. Table 1 and Table 5, part b).

In the case of TS of oxy radicals (Scheme II), the reduction of the charge on oxygen O^3, analogous to nitrogen N^3 of aminyl radicals (Scheme I), is not so pronounced. The character of oxygen O^1 which remains bound to the lactam carbon atom C^1 resembles the state of product complexes similarly to that in amino systems (Scheme I). The partial charge of the middle oxygen O^2 (shifted to oxy radical moiety) remains relatively low like in the reactant complex state.

Partial charges for the reaction center in product complexes do not exhibit any important irregularities (Table 5, part c). For methyl-substituted systems (Schemes I and II), both the MP2 and DFT methods give very similar electron distributions. Also, the comparison of the DFT electron distributions of methyl and phenyl systems in product complexes for both aminyl and oxy radical reactions shows large similarity (with the exception discussed above).

4. Conclusions

The main goal of this study was to find the molecular mechanism of termination of lactam peroxy radicals by the reaction with aminyl or oxy radicals. This reaction yields a cyclic imide from the lactam peroxyl, a hydro-

Table 5
Partial charge distribution (in e) in the reactant complexes, product complexes, and TS structures in the reaction of hexano-6-lactam peroxy radical with aminyl (I for methyl and I' for phenyl substituents) and oxy radicals (II for methyl and II' for phenyl substituents)

Reaction (method)	I (MP2)	I (DFT)	I′ (DFT)	II (MP2)	II (DFT)	II′ (DFT)
(a) Reactant complexes						
C^1	0.30	0.31	0.33	0.30	0.30	0.31
O^1	−0.30	−0.30	−0.42	−0.31	−0.30	−0.28
O^2	−0.19	−0.20	−0.24	−0.06	−0.07	−0.07
N^3/O^3	−0.21	−0.16	−0.16	−0.27	−0.24	−0.31
C^3	−0.31/−0.33[a]	−0.28/−0.29[a]	0.24/0.27[a]	−0.22	−0.19	0.36
(b) TS structures						
C^1	0.23	0.31	0.29	0.24	0.29	0.27
O^1	−0.19	−0.48	−0.47	−0.41	−0.40	−0.39
O^2	−0.56	−0.30	−0.34	−0.16	−0.16	−0.17
N^3/O^3	−0.03	0.04	−0.12	−0.15	−0.17	−0.24
C^3	−0.34/−0.33[a]	−0.32/−0.32[a]	0.26/0.24[a]	−0.24	−0.20	0.35
(c) Product complexes						
C^1	0.59	0.59	0.54	0.59	0.59	0.60
O^1	−0.48	−0.50	−0.46	−0.48	−0.49	−0.50
O^2	−0.58	−0.55	−0.55	−0.47	−0.44	−0.42
N^3/O^3	−0.28	−0.24	−0.37	−0.32	−0.30	−0.37
C^3	−0.30/−0.30[a]	−0.27/−0.27[a]	0.23/0.29[a]	−0.21	−0.18	0.37

[a] Methyl or phenyl close to/more distant from the lactam ring (cf. also Fig. 2).

xylamine from the aminyl radical, and a hydroperoxide from the oxy radical. Although chemical analysis of reaction products has safely proved this reaction course, it was difficult to figure out a reaction mechanism by which a hydroxy group is split off from a lactam peroxy radical.

This hypothesis was confirmed both by the MP2 method based on the molecular orbital approach, and by the DFT method (with one of the most reliable functionals- B3LYP).

We have found that in the first step, lactam peroxy radicals associate with aminyl or oxy radicals, respectively. On the reaction surface, the TS is localized nearer to the starting reaction components, concerning topology, charge distribution, and also the energy course of the whole process. At the stage of associates of final products, a cyclic imide is formed together with hydroxylamine from the aminyl radical or hydroperoxide from the oxy radical.

It was also found that the activation energies of the reactions proceeding in this way is very low. In the case of the reaction of a phenoxy radical with a lactam peroxy radical, even a zero-barrier reaction course can be considered.

It can be finally stated that for such a type of reactions, both the MP2 and DFT methods give very similar description.

Acknowledgements

The authors thank the Supercomputing Centers of the Charles University in Prague, of the Technical University in Prague, of the Masaryk University in Brno, and the West Bohemian University in Pilsen for the generous allotment of the CPU time. Financial support of the Grant Agency of Academy of Sciences of the Czech Republic (grant No. A4050702) and of the Grant Agency of the Charles University in Prague (grant No. 156/1999/B) is gratefully acknowledged.

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