

# Modeling Hindered-Amine Light Stabilizer-Promoted Polymer Stabilization: Computational Insight into the Mechanism for Nitroxyl Radical Regeneration from Aminoethers

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**Abstract:** A B3LYP computational study of the reaction of a methylperoxy radical with alkyl aminoethers has been performed, which represents a key step in polymer stabilization promoted by hindered-amine light stabilizers (HALS). In the most realistic model studied, a nitrogen oxidation mechanism is favored with respect to the S<sub>H2</sub> process known as the Denisov reaction. Nonetheless, the activation energy difference for the two reactions is less than 3 kcal/mol. We suggest that both mechanisms contribute to HALS-promoted polymer stabilization.

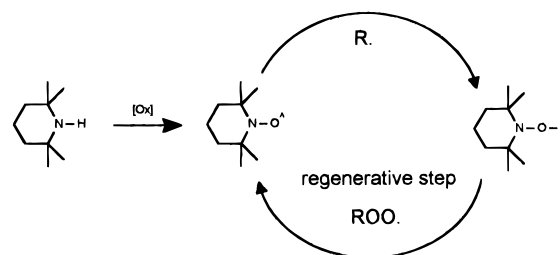
## Introduction

Polymer stabilization is one of the technological applications of chemistry that has a broad influence on everyday life. The derivatives of 2,2,6,6-tetramethylpiperidine known as hindered-amine light stabilizers (HALS) are among the most efficient polymer stabilizers known.<sup>1</sup> The mechanism of HALS stabilization has been extensively studied, but the results are still not conclusive. Scavenging of radicals is generally considered to be the mechanism by which HALS inhibit polymer autoxidation. In fact, HALS are spontaneously oxidized inside the polymer matrix to nitroxyl radicals,<sup>2,3</sup> which trap free carbon radicals, forming O-alkyl hydroxylamine derivatives.<sup>4</sup>

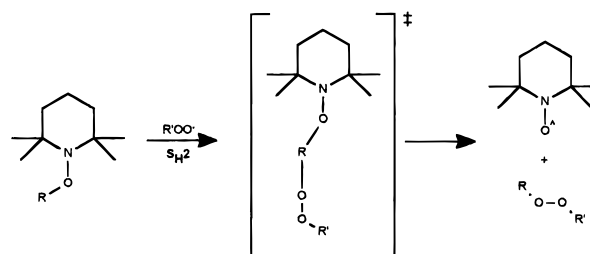
It has been shown that each HALS molecule is able to break several radical chains,<sup>2,5</sup> behaving as “inhibition catalysts”, as opposed to other stabilizers, such as hindered phenols, which trap radicals stoichiometrically.<sup>6</sup> This feature has been explained with the ability of the aminoethers to convert back to nitroxyls by reacting with alkylperoxy radicals (ROO•).<sup>7</sup> The process is often called the Denisov cycle (see Scheme 1).

It should be pointed out that the process sketched above is an oversimplification, since in the polymer stabilization process many other reactions and diffusion processes play important roles.<sup>8</sup> However, the stabilizing performance of a HALS is considered to be related to the efficiency of the regenerative step.

Scheme 1. Mechanism of HALS Stabilization



Scheme 2. The S<sub>H2</sub>-C Reaction



Three main regeneration mechanisms for the reaction of aminoethers with alkylperoxy radicals have been proposed in the literature:

(a) The bimolecular homolitic substitution (S<sub>H2</sub>) on carbon (S<sub>H2</sub>-C), where the NO-regeneration step is an alkylperoxy radical attack to the α-carbon of the aminoether, forming the nitroxyl radical and an alkyl peroxide. This mechanism is also known as the Denisov reaction<sup>1</sup> (see Scheme 2).

(b) The nitrogen oxidation mechanism,<sup>9</sup> where the alkylperoxy radical attacks the nitrogen of the aminoether, forming an oxidized tetracoordinated nitrogen intermediate. This intermediate then undergoes an α-hydrogen abstraction and a N–O bond cleavage to produce the nitroxyl radical, a carbonyl compound,

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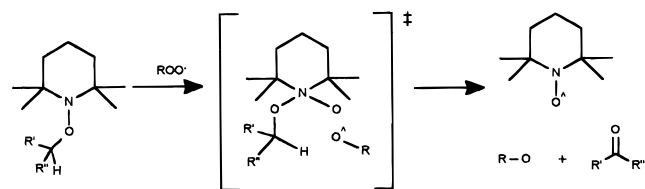
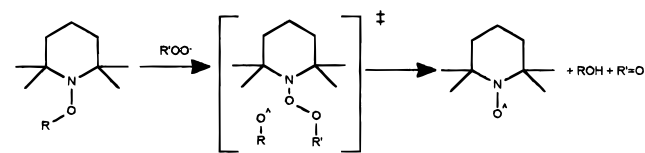
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**Scheme 3.** The Nitrogen Oxidation**Scheme 4.** The S<sub>H</sub>2-N Reaction

and an alcohol (see Scheme 3). The first proposal<sup>9a</sup> of this mechanism suggested the intermediacy of an ionic couple formed by a nitrogen-containing radical cation and an alcoholate anion, while in a later refinement,<sup>9b</sup> a concerted mechanism has been suggested.

(c) The S<sub>H</sub>2 on the nitrogen (S<sub>H</sub>2-N),<sup>10</sup> where the alkylperoxy radical attacks the nitrogen of the aminoether, with the formation of aminoperoxyether and alkoxy radical intermediates, which further evolve into a nitroxyl radical, an alcohol, and a carbonyl compound (see Scheme 4).

Experiments with labeled aminoethers<sup>9</sup> support the nitrogen oxidation hypothesis against the displacement mechanisms. This scheme requires that at least an hydrogen atom is present on the carbon in the  $\alpha$  position to the oxygen, thus excluding that regeneration will occur for tertiary radical-derived aminoethers. Nevertheless, HALS also show stabilizing properties for polymers such as polypropylene and polystyrene, where this kind of aminoethers are presumably formed during the stabilization cycle.

A computational study of the possible regeneration mechanisms could provide useful insight, but to our knowledge, only a semiempirical AM1 study on a very small model system has so far been performed.<sup>10</sup> Therefore, a more detailed computational investigation of the reaction of the methylperoxy radical with aminoethers is carried out in this paper.

**Computational Details**

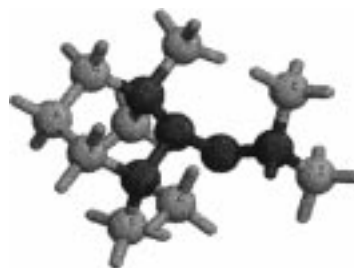
In this work, the reaction of a methylperoxy radical with two different model aminoether systems has been considered: a simple dimethyl-amino methyl ether (**S**) and a more realistic *N*-isopropoxy tetramethylpiperidine (**L**). This latter model simulates the aminoethers generated in a polymer, such as polyethylene, from the carbon radical trapping by tetramethylpiperidine nitroxyl (TEMPO), the prototypical HALS. For both systems, the hybrid density functional B3LYP<sup>11</sup> has been used, but with different basis sets. The 6-31G\*<sup>12</sup> basis has been used for all the atoms in **S**. For the **L** model, the 6-31G\* basis set has been used for the methylperoxy radical and for the atoms which are common to both aminoethers, that represent the most chemically relevant region of the system (darker atoms in Chart 1); the small STO-3G<sup>13</sup> basis set is used for all the remaining carbon and hydrogen atoms (lighter atoms in Chart 1).

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**Chart 1**

Using such a composite basis set, the smaller system (**S**) can be considered to be “embedded” in the larger one. This dual-level approach is similar in spirit to other multiple-level approaches, such as IMOMO,<sup>14</sup> CCSS,<sup>15</sup> and ONIOM<sup>16</sup> methods, where the system is divided into subsections, and the most accurate level is used to describe the most chemically relevant section, while the remaining subsections are described using less accurate, but also less computationally demanding, levels of theory. We will refer to this level of theory as B3LYP/EMBED for the rest of the paper.

The most stable axial and equatorial conformers of the TEMPO aminoether have been selected by using the systematic search method together with the MMFF-94<sup>17</sup> force field as implemented in Spartan 5.0.<sup>18</sup> All the B3LYP calculations have been performed using the Gaussian 94<sup>19</sup> package.

**Results and Discussion**

For the smaller model system **S**, three reaction paths have been found, corresponding to all three proposed mechanisms. The most favored transition state (**S5** in Figure 1) is associated with the S<sub>H</sub>2-N path, with a calculated activation energy of 29 kcal/mol, while the S<sub>H</sub>2-C and the nitrogen oxidation transition states (**S2** and **S3** in Figure 1) lie at 34 and 31 kcal/mol, respectively (see Table 1). It should be pointed out that, for both the nitrogen oxidation and the S<sub>H</sub>2-N paths, intrinsic reaction coordinate (IRC)<sup>20</sup> calculations show that the nitroxyl radical regeneration is not a concerted process. This means that the first step of both of these mechanisms produces intermediates. However, this is not kinetically relevant, since the alkoxy radical produced can readily extract a hydrogen atom, presumably from the newly generated oxyaminoether (**S4**) or aminoperoxyether intermediates, to produce nitroxyl radical, methanol, and formaldehyde, the proposed products of the reaction. The IRC calculation also shows that the nitrogen oxidation pathway

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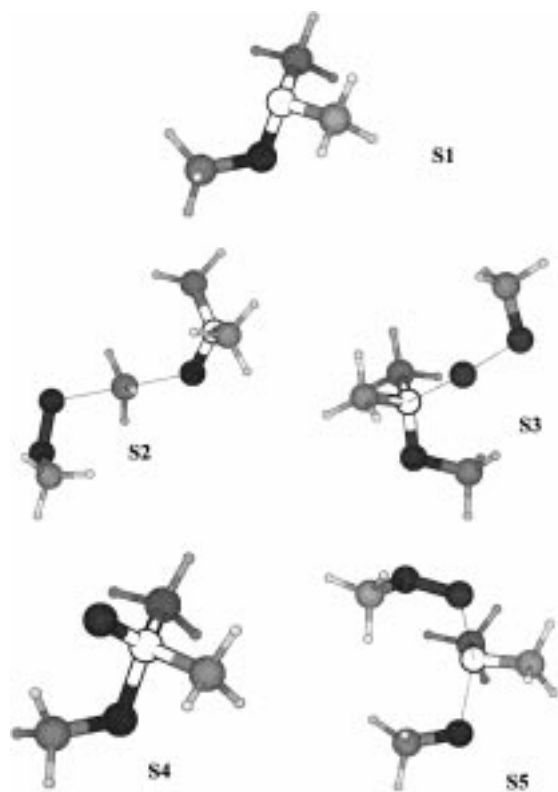
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**Figure 1.** Calculated structures (B3LYP/6-31G\*) of the most relevant stationary points on the potential energy surface for the methylperoxy radical + dimethylamino methyl ether system (S).

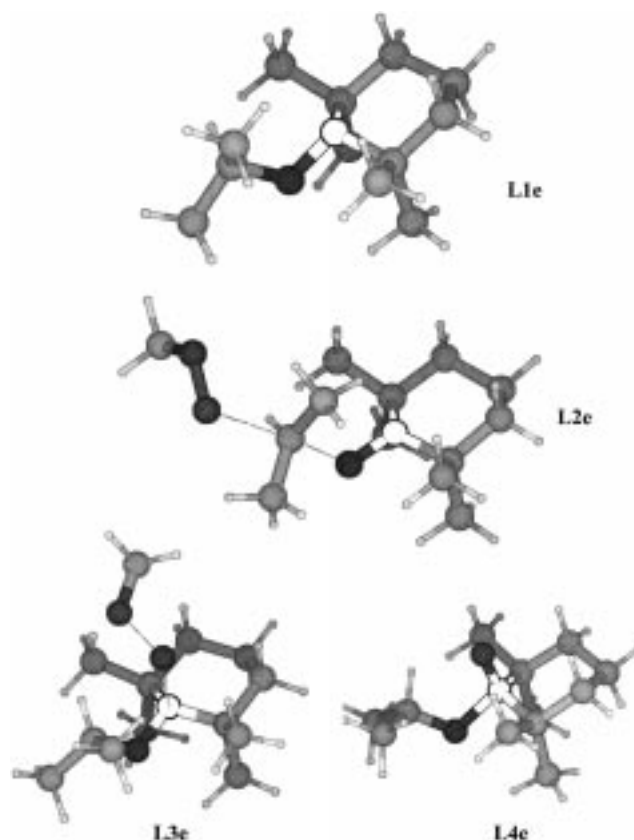
**Table 1.** B3LYP Energies (hartrees) and Energy Differences (kcal/mol) for the Methylperoxy Radical + Dimethylamino Methyl Ether System (S)

	B3LYP/6-31g*	
	<i>E</i>	$\Delta E$
<b>S1</b> + CH <sub>3</sub> OO	-439.857 441	0.0
<b>S2</b> (TS)	-439.807 618	34.1
(CH <sub>3</sub> ) <sub>2</sub> NO + CH <sub>3</sub> OOCH <sub>3</sub>	-439.878 076	-13.0
<b>S3</b> (TS)	-439.803 114	31.2
<b>S4</b> + CH <sub>3</sub> O	-439.859 000	-1.0
<b>S5</b> (TS)	-439.810 863	29.2
(CH <sub>3</sub> ) <sub>2</sub> NOOCH <sub>3</sub> + CH <sub>3</sub> O	-439.829 541	17.5

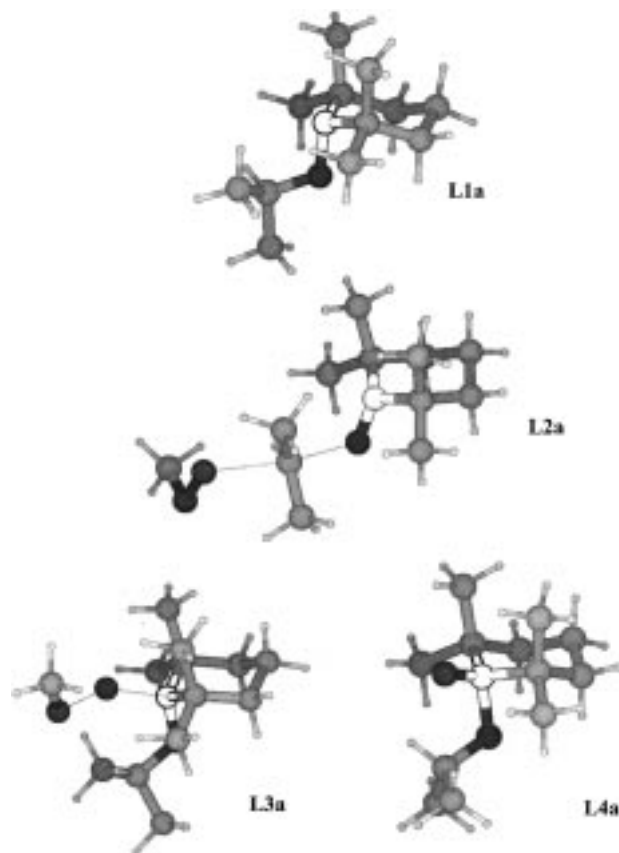
does not generate an ionic couple, as originally proposed by Klemchuck *et al.*,<sup>9a</sup> but generates instead the neutral oxyaminoether and methoxy radical molecules. It can be argued that ion separation requires stabilizing solvent-ion interactions in order to be achieved. These interactions are nonexistent in the simulation condition (gas phase), but they should also be small in polymers such as polyolefins, which have a dielectric constant around 2.5, so we do not believe that this finding is an artifact of the simulation.

The situation is different for the larger, and more realistic, model **L** (see Figures 2 and 3). Here, only two competing reaction paths for each TEMPO aminoether conformer (equatorial and axial) have been found, corresponding to the Denisov (**L2e** and **L2a** transition states) and the nitrogen oxidation (**L3e** and **L3a** transition states) mechanisms, the latter being favored ( $\Delta E^\ddagger \approx 2.5$  kcal/mol) (see Table 2).

Despite an extensive search, no reaction pathway has been found for the S<sub>H</sub>2-N mechanism, which is the most favored one in the **S** system. The TEMPO aminoether system shows no tendency at all to lose a methoxy radical upon the methylperoxy radical attack on the nitrogen; instead, the O-O bond breaks



**Figure 2.** Calculated structures (B3LYP/EMBED) of the most relevant stationary points on the potential energy surface for the methylperoxy radical + (equatorial) tetramethylpiperidylamino isopropyl ether system (**L<sub>e</sub>**).



**Figure 3.** Calculated structures (B3LYP/EMBED) of the most relevant stationary points on the potential energy surface for the methylperoxy radical + (axial) tetramethylpiperidylamino isopropyl ether system (**L<sub>a</sub>**).

**Table 2.** B3LYP Energies (hartrees) and Energy Differences (kcal/mol) for the Methylperoxy Radical + Tetramethylpiperidylamino Isopropyl Ether System (**L**)

	B3LYP/EMBED	
	<i>E</i>	$\Delta E$
Equatorial Paths		
<b>L1e</b> + CH <sub>3</sub> OO	-787.346 011	0.0
<b>L2e</b> (TS)	-787.298 203	30.0
Ipr-OOCH <sub>3</sub> + TEMPO	-787.382 390	-22.8
<b>L3e</b> (TS)	-787.302 112	27.5
<b>L4e</b> + CH <sub>3</sub> O	-787.351 444	-3.4
Axial Paths		
<b>L1a</b> + CH <sub>3</sub> OO	-787.346 855	-0.5
<b>L2a</b> (TS)	-787.293 373	33.0
Ipr-OOCH <sub>3</sub> + TEMPO	-787.382 390	-22.8
<b>L3a</b> (TS)	-787.298 994	29.5
<b>L4a</b> + CH <sub>3</sub> O	-787.351 595	-3.5

and nitrogen oxidation occurs, according to the nitrogen oxidation mechanism. This can be rationalized by observing the geometry of the S<sub>H2</sub>-N transition state in the **S** system (**S5**): the aminoether nitrogen has an sp<sup>2</sup> hybridization, and the ONO angle is very wide, as required for an S<sub>H2</sub> attack at the nitrogen. In the **L** system, these geometrical requirements would force both the methylperoxy radical and the alkoxy leaving group between the four methyl substituents of the piperidine ring, with a large increase in the steric repulsion. Even for the **L** model, the IRC calculation showed that the nitrogen oxidation mechanism is not concerted and produces neutral intermediates (**L4e** and **L4a**), just like in the small **S** model.

It is intriguing to observe that, on going from the **S** to the **L** system, the increased steric hindrance on the  $\alpha$ -carbon does not appear to disfavor the Denisov mechanism, which, in turn, appears to be *stabilized* by the extra methyl substituents, since the barrier goes down from the 34 kcal/mol of the **S** model to the 30 kcal/mol of the **L** model. A possible explanation for this

behavior can be derived from the observation that, in the transition state, the  $\alpha$ -carbon possesses a significant radical character (unpaired spin density around 0.2). Thus, any substituent on the  $\alpha$ -carbon, such as the methyl group, that has the ability to stabilize an  $\alpha$ -radical will also have a stabilizing effect the S<sub>H2</sub>-C transition state. It is also conceivable that the presence of better radical-stabilizing substituents on the  $\alpha$ -carbon can further stabilize the S<sub>H2</sub>-C pathway and even reverse the balance between the two mechanisms, favoring the direct displacement with respect to nitrogen oxidation. This situation may occur in polymers where allylic and benzylic radicals are formed in the autoxidation process, e.g., polybutadiene and polystyrene. Further investigation on this subject is in progress.

### Conclusions

A computational study on two model systems has been able to identify that two possible reaction mechanisms are relevant to the nitroxy radical regeneration. These two paths correspond to an S<sub>H2</sub> attack on the  $\alpha$ -carbon of the aminoether and to a nitrogen oxidation mechanism. Both mechanisms show a substantial barrier ( $E^\ddagger > 27$  kcal/mol). The most favored path corresponds to a nitrogen oxidation mechanism, as first proposed by Klemchuck et al.; nonetheless, the calculated activation energy difference between the two paths is not large (2.5 kcal/mol) in the most realistic model studied. Furthermore, by comparing the results for the two models, it also appears that increased alkyl substitution at the  $\alpha$ -carbon is not detrimental to the direct displacement mechanism, despite the increased steric hindrance. We suggest that both regeneration mechanisms contribute to HALS-promoted polymer stabilization.

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