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New Insights into the Mechanism of Amine/Nitroxide Cycling during the Hindered Amine Light Stabilizer Inhibited Oxidative Degradation of Polymers

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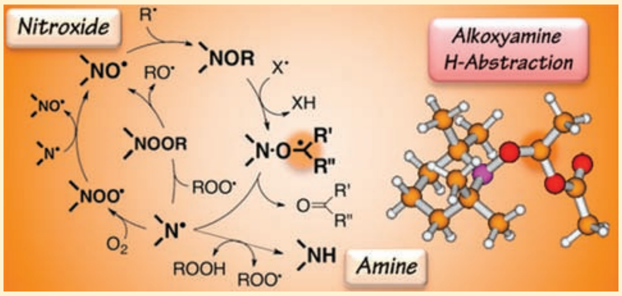
Ⓢ *Supporting Information*

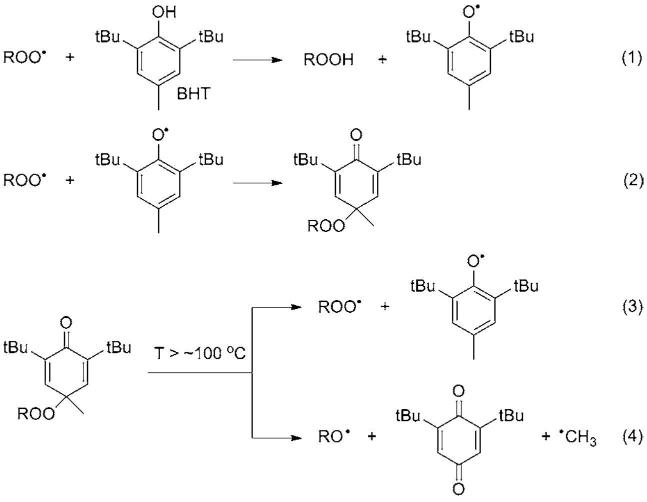


ABSTRACT: High-level ab initio molecular orbital theory calculations are used to identify the origin of the remarkably high inhibition stoichiometric factors exhibited by dialkylamine-based radical-trapping antioxidants. We have calculated the free energy barriers and reaction energies at 25, 80, and 260 °C in the gas phase and in aqueous solution for a broad range of reactions that might, potentially, be involved in amine/nitroxide cycling, as well as several novel pathways proposed as part of the present work, including that of *N*-alkyl hindered amine light stabilizer activation. We find that most of the literature nitroxide regeneration cycles should be discarded on either kinetic or thermodynamic grounds; some are even inconsistent with existing experimental observations. We therefore propose a new mechanistic cycle that relies on abstraction of a *β*-hydrogen atom from an alkoxyamine ($R^1R^2NOCHR^3R^4$). Our results suggest that this cycle is energetically feasible for a range of substrates and provides an explanation for previously misinterpreted or unexplained experimental results. We also explore alternative mechanisms for amine/nitroxide cycling for cases where the alkoxyamines do not possess an abstractable *β*-hydrogen.

■ INTRODUCTION

Radical-trapping antioxidants (RTAs) retard the oxidative degradation of organic materials.[1] The two main classes of RTAs are phenols and amines, only the former being employed in nature for this purpose in living organisms (vitamin E),[2] whereas both are utilized to protect a wide variety of commercial products. The mechanism by which phenols exert their antioxidant properties is firmly established[3] and is illustrated in Scheme 1 for the most commercially important of these, viz., 2,6-di-*tert*-butyl-4-methylphenol (BHT). At temperatures below ca. 100 °C, each molecule of this phenol traps two of the chain-carrying peroxyl radicals, $ROO^\bullet$, and thereby terminates two oxidation chains; i.e., the stoichiometric factor for inhibition, *n*, is 2.0. At higher temperatures, phenols become increasingly ineffective antioxidants with *n* dropping toward zero as the temperature is increased. This is because the peroxycyclohexadienone, formed by coupling of the phenoxyl and peroxyl radicals, is thermally unstable, breaking down to form radicals, which will continue the chain (reactions 3 and 4).

Scheme 1. Antioxidant Action of BHT



For amine RTAs the situation is far more complex. It is helpful to distinguish diarylamine antioxidants from dialkylamine antioxidants. Diarylamines, Ar_2NH, retard oxidation by donating their *NH* hydrogen atom to an $ROO^\bullet$ radical (reaction 5 in Scheme 2).[4] At temperatures below ca. 100 °C, diarylamines have, like phenols, *n* values of about 2.0. However, the inhibition chemistry now diverges from that of phenols with the diarylaminyl radical, $Ar_2N^\bullet$, being converted into a diaryl nitroxide radical, $Ar_2NO^\bullet$.[5,6] These nitroxides are

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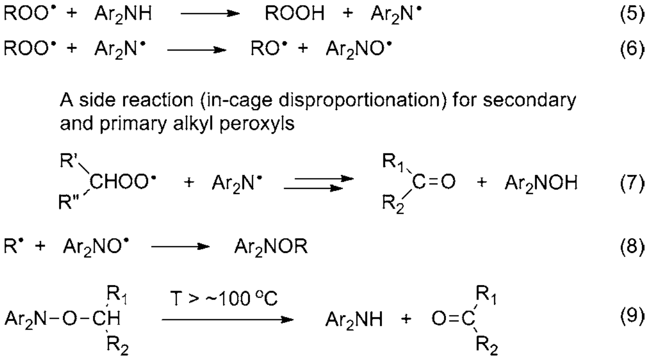
Scheme 2. Activation and JKZG Regeneration Cycle of Diarylamine Antioxidants

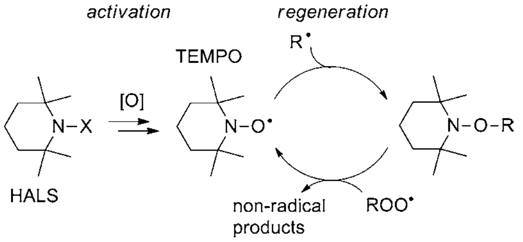


formed by reaction of the aminyl radical with a peroxyl radical (reaction 6, not with oxygen),[7] and their yields are lower in those substrates that oxidize via secondary or primary alkyl peroxyl radicals because of an in-cage disproportionation (reaction 7).[6] Although the $Ar_2NO^\bullet$ radicals can react with $ROO^\bullet$ (with oxidation of an aryl ring),[8,9] they are mainly captured by carbon-centered radicals, $R^\bullet$, from the substrate to form *N,N*-diarylalkoxyamines, Ar_2NOR (reaction 8).

The most intriguing thing about diarylamine antioxidants is that (in contrast to phenols) at temperatures >100 °C their n values *increase* (rather than decrease) and can reach quite substantial values, e.g., $n = 40$ for diphenylamine in a paraffin oil oxidizing at 130 °C.[9] A number of mechanisms have been hypothesized for this process, most of them being mainly of historical interest. The critical clue to the chemistry accompanying these high stoichiometric factors was provided by Jensen, Korcek, Zinbo, and Gerlock (JKZG),[10] who showed that the diarylamine was formed during the thermal decomposition of the alkoxyamine (reaction 9). This is thought to occur via N—OR bond homolysis,[11] followed by an in-cage disproportionation of the N- and O-centered radicals to give an amine and a carbonyl product, a reaction that will be increasingly favored in highly viscous polymeric materials which impose very large "cage effects" on geminate radical pairs. The diarylamines so formed then re-enter the JKZG catalytic cycle (reaction 5), a cycle that disposes of two substrate-derived free radicals ($R^\bullet$ and $ROO^\bullet$) on every turn.[10]

However, the products of diarylamine oxidation are very intensely colored, an undesirable attribute that precludes their use in many applications except where color is not an issue (e.g., in engine lubricating oils). In most other applications, product formulators generally turn to dialkylamines, specifically to di-*tert*-alkylamines,[12] and various derivatives thereof. These are generally based on 2,2,6,6-tetramethylpiperidine (TEMPH) and are known in the trade as hindered amine light stabilizers, or HALSs.[13] For many polymeric materials HALSs are remarkably effective antioxidants both at the high temperatures of processing[14] and at the much lower temperatures of use. HALSs are particularly effective for outdoor applications where the organic substrate would otherwise undergo photoinduced oxidative degradation. The importance of HALSs in the modern world is emphasized by the following quotation from a recent review:[13] "Without the discovery of HALS, the outdoor applicability of many polymers would be limited." However, despite their widespread use, the catalytic process by which HALSs protect materials from oxidative damage, and the nature of the side reactions that disrupt this process, remains a topic of debate. The commonly accepted scheme (known as the Denisov cycle)[15] involves initial conversion of HALSs to the corresponding nitroxide. This nitroxide then traps a carbon-centered radical to form an alkoxyamine, which somehow "regenerates" the nitroxide (see Scheme 3).

Scheme 3. Denisov Cycle



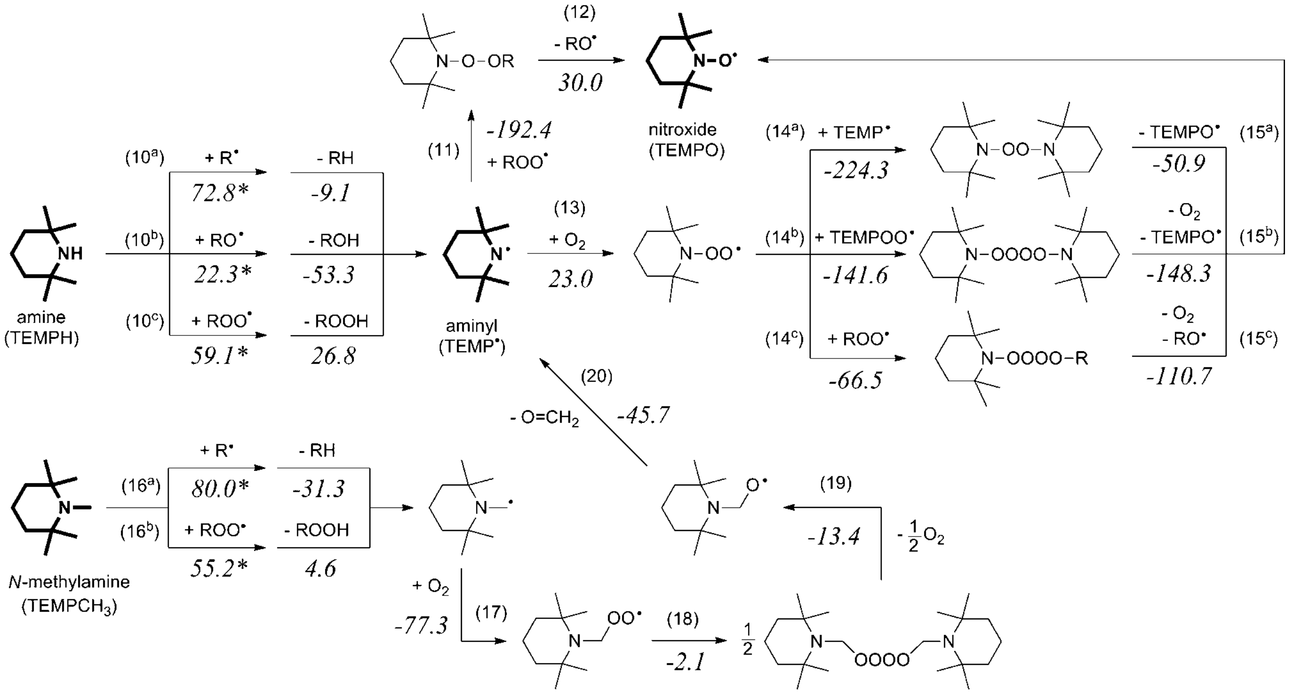
However, the Denisov cycle's precise mechanism remains unclear. First, the mechanism of *activation* of the initial HALS will be dependent on the chemical structure of its X group. This process is often described only in general terms, not in mechanistic detail.[15−17] Second, more than a dozen different pathways (comprising over 30 individual reactions, many with no established precedent!) have been proposed to contribute to, or interfere with, the *regeneration* part of the Denisov cycle.[18−20] In a preliminary attempt to bring chemical rigor to regeneration, one of us recently employed high-level ab initio molecular orbital theory to evaluate the kinetics and thermodynamics of many of these proposed mechanisms using the nitroxide (2,2,6,6-tetramethylpiperidin-1-yl)oxyl ($TEMPO^\bullet$) and two model radicals (based on species present in degrading polyethylene and polyester).[21] Many of the proposed mechanisms were quickly discounted, and of those considered, the kinetically and thermodynamically preferred pathway was that proposed by Klemchuk.[19] However, even this mechanism of regeneration is still improbable because of a seemingly insurmountable activation barrier (~150 kJ mol^{-1}) for one of its key steps.[21] Perhaps more importantly, Klemchuk's pathway does not account for the experimentally detected formation of the secondary piperidines, e.g., TEMPH in the decomposition of $TEMPO^\bullet$-based HALSs under thermo- and photo-oxidative conditions.[19,22,23] Although some side reactions leading to amines have been suggested previously (e.g., by Barton[20]), these were also shown to be energetically implausible in our earlier theoretical study.[21]

Thus, there would appear to be a significant gap in our understanding of the reactions of nitroxide radicals with polymers and other organic materials. This "gap" has implications not only for the design of more effective HALSs, but also for other important applications of aliphatic nitroxides, including their use as medicinal antioxidants,[24] spin traps,[25] and control agents in nitroxide-mediated living radical polymerization (NMP).[26] In an attempt to "plug the gap", we have used high-level ab initio molecular orbital theory to search for a new, and more believable, mechanism for amine/nitroxide cycling that would account for all the experimental observations.

■ COMPUTATIONAL METHODOLOGY

Standard ab initio molecular orbital theory and density functional theory calculations were carried out using Gaussian 09[27] and MOLPRO 2009.1.[28] The level of theory was chosen on the basis of our prior assessment studies for the study of nitroxide radical chemistry; in those studies these procedures were demonstrated to

Scheme 4. Thermal Activation of Secondary HALSs and Tertiary *N*-Methyl-HALSs[a]



[a]Numbers in italics are calculated Gibbs free energies (kJ mol^{-1}, gas phase, 25 °C) of the reactions and activation (denoted by an asterisk).

deliver results to within chemical accuracy (ca. 5 kJ mol^{-1} for bond dissociation energies, 0.050 V for redox potentials).[11,29,30] The methodology has also been successfully benchmarked for the kinetics and thermodynamics of other radical reactions.[31] Except where otherwise noted, all mechanisms were tested for the case of TEMPO$^\bullet$ reacting with the typical radical species found in a degrading polyester to be consistent with the recent experimental study[23] and to allow direct comparison with our earlier computational results.[21] Calculations on radicals were performed with an unrestricted wave function except in cases designated with an "R" prefix where a restricted open-shell wave function was used. For all species, either full systematic conformational searches (at a resolution of 60°) or, for more complex systems, energy-directed tree searches[32] were carried out to ensure that global, and not merely local, minima were located. The geometries of all species were fully optimized at the B3-LYP/6-31G(d) level, and the frequencies were also calculated at the same level and scaled by recommended scale factors.[33] All transition-state geometries were characterized by a single imaginary frequency.

Accurate energies for all species were then calculated using a double-layer ONIOM-type method. The core layer was calculated at the G3(MP2)-RAD[34] level of theory, whereas RMP2/6-311+G-(3df,2p) was applied to the full system. This methodology has been previously tested against experimental data for nitroxide radical trapping[11] and nitroxide redox chemistry.[29] For some species (e.g., trioxides and O-centered radicals) UCCSD(T)-RHF calculations in MOLPRO 2009.1 were associated with T1 diagnostics slightly higher than 0.02—a reference value above which a multireference treatment should be considered. However, due to their size, an accurate multireference treatment (including dynamic correlation as well as static correlation) was not feasible. Instead, we performed additional UCCSD(T)-UHF calculations for these species to provide a comparison with the UCCSD(T)-RHF calculations. Although both procedures are single reference, if multireference effects have a significant impact on the energies, we would expect the two procedures to show some differences due to the ability of the UCCSD(T)-UHF calculations to "mimic" a multireference wave function through spin contamination. In each case, we find that all obtained energies are very close (within 0.2 kJ mol^{-1}) to the UCCSD(T)-RHF energies. As a further check, for a number of "problematic" O-centered radicals from this study, we have calculated dissociation energies of the corresponding O−H bonds using another high-level composite method, G4(MP2)-6X,[35] which was recently shown to be very accurate in reproducing experimental bond dissociation and radical stabilization energies.[36] These results were compared with the G3(MP2)-RAD values and available experimental data.[37] In general, we found insignificant differences between the two theoretical procedures (within 7 kJ mol^{-1}), with both methods reproducing the experiment to within chemical accuracy (mean absolute deviation <5 kJ mol^{-1}). This indicates that these borderline multireference systems are sufficiently well described by our single-reference wave functions and hence that our mechanistic conclusions should not be affected (see Appendix 1 in the Supporting Information for details).

Gas-phase entropies and thermal corrections at 25, 80, and 260 °C were calculated using standard textbook formulas[38] for the statistical thermodynamics of an ideal gas under the harmonic oscillator approximation in conjunction with the optimized geometries and scaled frequencies. Gibbs free energies of activation[39] and reactions were computed using the Gibbs fundamental equation. Free energies of solvation (in aqueous conditions) were then calculated using the polarized continuum model (PCM)[40] at the B3-LYP/6-31G(d) level of theory. Free energies of each species in solution at 25 °C were calculated as the sum of the corresponding gas-phase free energy and the obtained free energy of solvation and corrected for the phase change correction term $RT(\ln V)$. However, because consideration of the higher temperature and the bulk solvent did not introduce any substantial change to the gas-phase data, only the gas-phase results at 25 °C are given here (see the Supporting Information for the 80 and 260 °C and solution-phase data).

The Gibbs free energies of activation for reactions that involved proton transfer were corrected for the effects of tunneling according to the standard textbook formula[41]

$$\Delta G^{\ddagger}_{\text{eff}} = \Delta G^{\ddagger} - RT \ln \kappa(T) \qquad (1)$$

In this formula, $\kappa(T)$ is the tunneling correction factor, T is the absolute temperature, R is the universal gas constant, and $\Delta G^{\ddagger}$ is the Gibbs free energy of activation.[42] The tunneling coefficient $\kappa(T)$ corrects for quantum effects in motion along the reaction path. In this work, Eckart tunneling coefficients[43] were evaluated using the imaginary frequency as an estimate of the curvature of the potential energy surface, as described previously.[44]

■ RESULTS AND DISCUSSION

A plausible mechanism for the antioxidant activities of HALSs requires answers to two questions: (i) What are the mechanisms of nitroxide activation and regeneration? (ii) How is the amine formed? That is, is it formed via some competitive side reaction or as an intermediate in the nitroxide regeneration cycle itself? To address these questions, we have used high-level ab initio molecular orbital theory calculations to compare the kinetics and thermodynamics of alternative literature pathways of nitroxide activation and regeneration and amine formation and compared these with new mechanisms proposed in this work. The chemical model and the computational methodology in the present study were chosen to match those of our previous study of the Denisov cycle.[21] TEMPO$^•$ represents the nitroxide moiety formed from a typical HALS, and R$^•$ = $CH_3CH^•OC(O)CH_3$ serves as a model polyester-derived radical.[23,45] The complete set of calculated energetic parameters for all reactions studied in the present work and the normalized energy profiles for all considered pathways are given in Appendix 2 of the Supporting Information. Below we present and discuss in turn our search for plausible mechanisms for activation, amine formation, and regeneration. In the two latter cases, we first evaluate existing literature proposals before presenting a new catalytic cycle for HALSs that not only is more energetically feasible than the literature alternatives, but simultaneously accounts for amine formation and other previously unexplained experimental observations.

Activation. As noted in the Introduction, there is a lack of mechanistic understanding of how an initial stabilizer is transformed into its nitroxide and how this process is affected by the structure of the stabilizer itself. Historically, the first HALSs were either the secondary amines themselves (e.g., Tinuvin770 and Hostavin3050) or their more basic *N*-methyl derivatives (e.g., Tinuvin292 and Tinuvin765). A number of mechanisms for such a transformation of secondary amine HALSs into nitroxides have been proposed (see Scheme S1 in the Supporting Information),[46] but most of these are solely of historical interest due to the improbable structures of their intermediates and transition states. A more widely accepted mechanism of secondary HALS activation involves a H-atom abstraction by various reactive polymeric radicals, for example, ROO$^•$ (see Scheme 4, reaction 10^c).[17,47] Clearly, this reaction is much less thermodynamically favored and considerably slower for aliphatic secondary amines than for diarylamines (reaction 5). However, under photo-oxidative conditions, the formation of TEMP$^•$ from TEMPH may occur via a dioxygen/TEMPH charge transfer complex.[16,47] Once the aminyl radical[48] has formed, it will rapidly be oxidized to the corresponding nitroxide. We have considered a number of possible mechanisms of this transformation (see Scheme S2 and Table S4 in the Supporting Information). On the basis of both our results and experimental measurements,[47] the most likely possibility is that TEMP$^•$ moieties in polymers are converted into TEMPO$^•$ moieties in the same way that the diarylamine antioxidants are converted into their nitroxides (Scheme 2), i.e., via formation and subsequent decomposition of an *O*-alkylperoxyamine (reactions 11 and 12 of Scheme 4). Additionally, the aminyl radical could be oxidized via addition of dioxygen (reaction 13) followed by loss of the outer oxygen atom (TEMPOO$^•$) via reaction with a second radical (reactions 14 and 15).[18f,47]

Conversion of *N*-methyl-HALSs into their nitroxides is assumed to involve formation of the TEMPH and/or TEMP$^•$ moieties because their photostabilizing efficiencies are qualitatively similar to those of HALSs having secondary amine functionality.[13,17,49] Nevertheless, HALSs containing a tertiary amine functionality tend to provide better protection against polymer thermal degradation than those containing a secondary amine functionality.[50] This suggests that, in use, the tertiary amines provide a more stable “reservoir” of the active secondary amines than would be provided by an equal concentration of the secondary amines themselves. Tertiary HALSs are also better than secondary HALSs at retarding photooxidative degradation in part, at least, because of better quenching of singlet oxygen, a process that facilitates their transformation into secondary HALSs. During polymer thermal degradation, *N*-methyl-HALSs are activated in a radical pathway that yields a peroxyl radical (reactions 16 and 17). We have considered a number of processes that could account for both the HALS activation (i.e., overall conversion of a peroxyl radical to nitroxide) and the experimentally identified formation of the $TEMPH_2^+$ formate salt[17,46b,49] (for details see Scheme S3 and Table S4 in the Supporting Information). The most energetically plausible of these involves peroxyl radical dimerization, followed by decomposition of the tetroxide into two alkoxyl radicals that then undergo *β*-scission with the loss of formaldehyde and the formation of TEMP$^•$ (reactions 18–20). This last radical either will be oxidized to TEMPO$^•$ (as discussed above; see reactions 11–15) or will abstract hydrogen to yield TEMPH (reverse of reaction 10^c). Under free radical oxidizing conditions, the formaldehyde will be rapidly oxidized to formate, which will give the experimentally detected salt with TEMPH.

Nowadays most HALSs are alkoxyamines which facilitate formation of nitroxide radicals via direct NO–R homolysis; the structures of these alkoxyamines are therefore often designed in such a way that direct homolysis of the NO–R bond is preferred over that of the N–OR bond. To illustrate this, we have calculated the Gibbs free energies for homolysis of the N–OR and NO–R bonds for selected *N*-alkoxyamines, analogous to commercially available HALSs (Figure 1; for details see Table S5 in the Supporting Information). Our results indicate that in all cases studied here NO–R bond cleavage is thermodynamically favored over that of the N–OR bond. Similar results were also obtained at commercially relevant temperatures of 80 and 260 °C (see Figure S3 in the

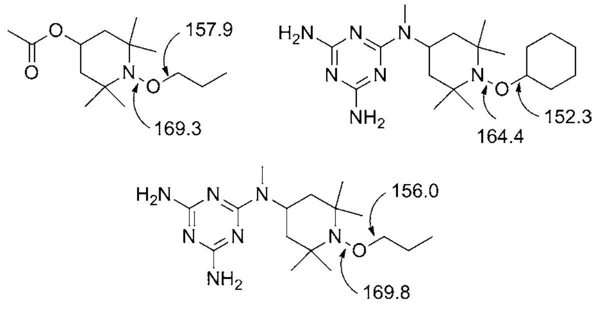


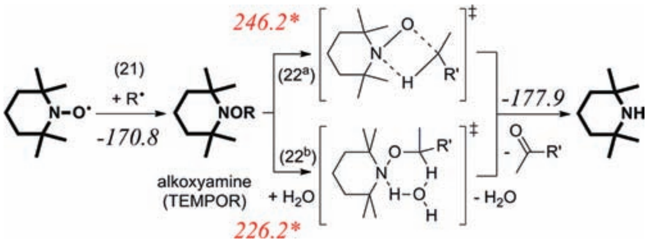
Figure 1. Gas-phase Gibbs free energies (kJ mol^{-1}, 25 °C) for N–OR and NO–R bond homolyses in model HALSs.

Supporting Information).[23] The photodecomposition of alkoxyamines has not been as thoroughly investigated as their thermal decomposition. However, it is worth noting that under UV photolysis an intramolecularly photosensitized ArR′NOR has been demonstrated by electron spin resonance (ESR) spectroscopy to undergo both N−OR and NO−R bond cleavage,[51,52] whereas in studies of alkoxydialkylamines (i.e., HALSs) only NO−R bond cleavage was observed (for details, see Scheme S4 and Table S6 in the Supporting Information).[51,52] Thus, direct homolysis of these HALSs will favor, though not necessarily exclusively, the formation of nitroxides rather than aminyl radicals.

Do Dialkylamines Cycle the Same Way as Diarylamines? The activation of aliphatic amines (reactions 10−12 in Scheme 4) appears to resemble that of aromatic amines (reactions 5 and 6 in Scheme 2). This raises the question of whether the JKZG cycle, previously proposed to account for nitroxide regeneration when diarylamines are used, might also be applicable to dialkylamine antioxidants. This cycle could also provide a convenient explanation for the formation of a secondary piperidine moiety, which, as noted in the Introduction, was detected in the thermal decomposition of TEMPO$^{\bullet}$-based HALSs at 120 °C (but not at lower temperatures).[22] Moreover, it was recently demonstrated that the HALS Tinuvin123 (bis(*N*-(octyloxy)-2,2,6,6-tetramethyl-4-piperidyl) sebacate) in a polyester-based metal coating yielded a product in which one *N*-ether piperidine moiety (*N*-OC_8H_{17}) had been converted to a secondary piperidine (*N*-H) at both 260 and 80 °C under irradiation with the full solar spectrum.[23] A secondary piperidine was also detected when *N*-(cyclohexyloxy)-2,2,6,6-tetramethyl-4-piperidinyl benzoate was added to cyclohexane under oxidative conditions at 60 °C.[19]

Activation of the initial HALS produces a nitroxide that rapidly scavenges a carbon-centered radical formed in the degrading polymer (reaction 21 in Scheme 5). Thermal decomposition of the resulting alkoxyamine TEMPOR and formation of the amine TEMPH is a crucial step if the JKZG cycle is to be "force-fitted" to HALSs (reaction 22, nominally analogous to Reaction 9 in Scheme 2). However, for TEMPOR such processes involve impossibly high activation barriers.

Scheme 5. Potential Alkoxyamine Decomposition to an Amine and a Carbonyl via Intramolecular H-Atom Transfer[a]



[a]Red color is used to indicate unfeasibly high activation barriers, which make this JKZG cycle improbable. Numbers in italics are calculated Gibbs free energies (kJ mol^{-1}, gas phase, 25 °C) of the reactions and activation (denoted by an asterisk).

Although TEMP$^{\bullet}$ is not expected to be formed as a result of a direct homolysis in the initial alkoxyamine HALSs, some very different alkoxyamines will be formed after their activation and trapping of polymer radicals, and these new alkoxyamines might serve as the aminyl radical (amine) source. Both experiment and theory indicate that N−OR cleavage is (relatively) more favored when the O−R bond is strengthened by effects arising from the presence of heteroatoms in the R group, e.g., anchimeric effects.[11,53] Such effects would be expected with some of the R$^{\bullet}$ radicals present in a degrading polyester. That is, NO−R bond cleavage is favored over N−OR cleavage by 50−60 kJ mol^{-1} for R_1 and R_2, but the two modes of scission are competitive for R_3 (Figure 2). Thus, direct N−OR homolysis of the alkoxyamine might be important for nitroxide/amine cycling in HALS-stabilized polyesters (it might also be an unrecognized side reaction in certain nitroxide-mediated polymerizations). Unfortunately, although this modified JKZG cycle just might play some small role during HALS-inhibited polyester degradation, it will be strongly disfavored for most (if not all) other types of polymers. Hence, some alternative mechanism(s) is (are) required to explain the experimentally observed regeneration of nitroxide and formation of amine.

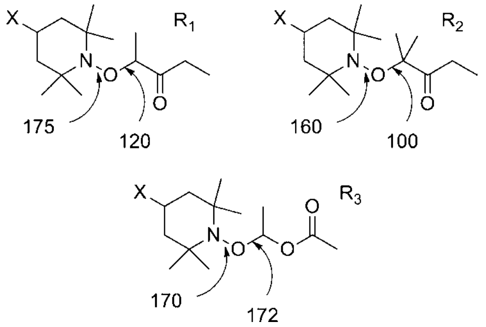


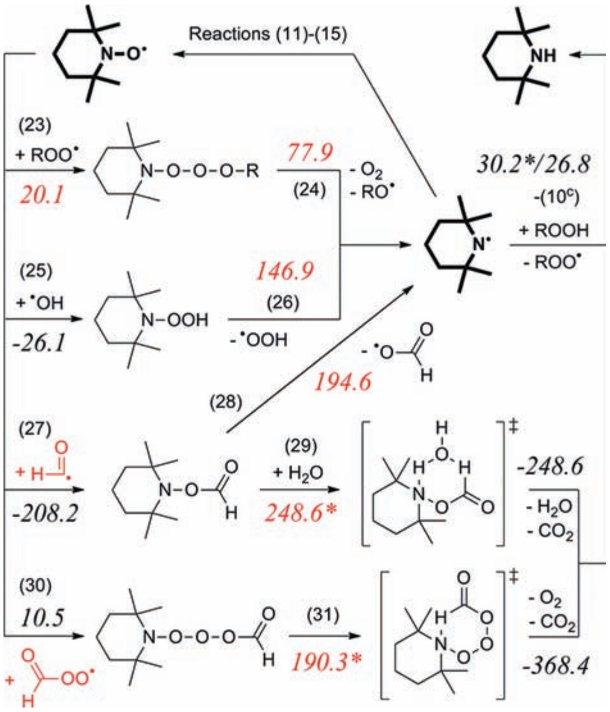
Figure 2. Model polyester radical fragments ($R_{1,2,3}$ with various substituents X in the piperidine moiety) and corresponding average gas-phase Gibbs free energies (kJ mol^{-1}, 25 °C) of N−OR and NO−R bond homolyses (see Figure S4 and Table S7 in the Supporting Information).

Can Other Literature Mechanisms Explain Nitroxide Regeneration and Amine Formation? Since HALS can, at best, only rarely participate in the JKZG cycle (Scheme 2), we consider in Scheme 6 a number of literature proposals for aminyl (and hence secondary amine) formation, including Barton's pathway via a trioxide (reactions 23 and 24),[20,21] Turro's mechanism via an amine hydroperoxide (reactions 25 and 26),[54] and some reactions with formyl-derived radicals, as suggested by Gerlock and co-workers for HALS-stabilized acrylic/melamine coatings (reactions 27−31).[55,56]

As is clear from Scheme 6, none of these mechanisms offer a realistic pathway for the TEMPO$^{\bullet}$ → TEMP$^{\bullet}$ transformation because of extreme activation barriers, highly thermodynamically disfavored steps, and/or the need for reagents that would be found only in a very limited number of polymers. (We refer readers interested in a more detailed discussion of each of these pathways to Appendix 5 in the Supporting Information.) Since literature mechanisms do not provide a regeneration cycle involving an intermediate aminyl radical, we sought alternatives.

We mentioned in the Introduction that Klemchuk's nitroxide regeneration pathway (reactions 32 and 33, Scheme 7)[19] was found in our earlier work to be the most energetically favored,[21] but it is nevertheless improbable due to an implausibly high activation barrier (reaction 32).[57] We therefore applied theory to evaluate the kinetics and thermodynamics of other suggested literature mechanisms of potential relevance to our goal but not previously applied to HALSs (see Scheme 7). The predecessor

Scheme 6. Literature Mechanisms of Nitroxide Regeneration and Amine Formation via an Aminyl Radical[a]

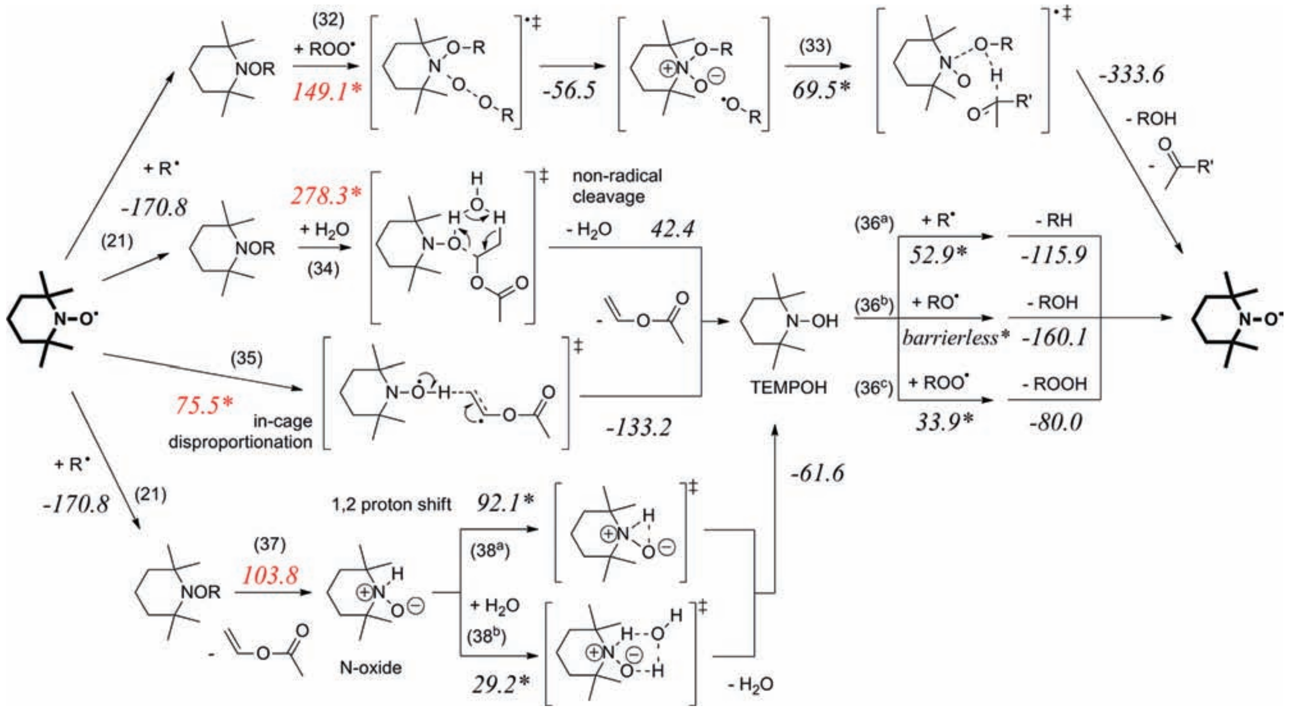


[a]Red color is used to indicate unfeasibly high activation barriers, highly endergonic reactions, and species found only in specific types of degrading polymers—factors which make these pathways improbable. Numbers in italics are calculated Gibbs free energies (kJ mol^{-1}, gas phase, 25 °C) of the reactions and activation (denoted by an asterisk).

of the JKGZ cycle for diarylamines is the BBF cycle proposed by Bolsman, Blok, and Frijns[58] (reactions 34–36 of Scheme 7). This pathway relies on a *β*-hydrogen atom transfer from R$^{\bullet}$ to TEMPO$^{\bullet}$ and can occur either via a nonradical alkene elimination from TEMPOR or an in-cage radical cross-disproportionation between R$^{\bullet}$ and TEMPO$^{\bullet}$.[59] However, the former process was found to have an insurmountable activation barrier,[60] while the latter is not energetically competitive with the recombination of R$^{\bullet}$ and TEMPO$^{\bullet}$ (reaction 21; also see normalized energy profiles in Figure S2A of the Supporting Information). Another potential mechanism of alkoxyamine transformation is similar to the Cope elimination of *N*-oxides (reactions 37 and 38).[61] However, its very first stage—formation of the *N*-oxide—is strongly disfavored thermodynamically compared with the alternative channels of alkoxyamine decomposition, which also makes this mechanism improbable. Therefore, none of the literature mechanisms investigated here or previously[21] provide a kinetically and thermodynamically plausible regeneration mechanism. Moreover, none of the pathways from Scheme 7 account for the experimentally observed formation of TEMPH analogues; various literature mechanisms of amine formation (via aminyl, Scheme 6), which could serve as possible side reactions to these regeneration cycles, were also discounted earlier.

Our Proposed Catalytic Cycle. A crucial difference between the mechanisms of antioxidant action of diarylamines and dialkylamines is that the latter yield alkoxyamines that *generally* do not decompose *thermally* to give aminyl radicals (and, hence, amines). Therefore, dialkylamines do not, generally, cycle by the JKZG mechanism (originally proposed to explain the high antioxidant activity of diarylamines in lubricating oils at elevated temperatures).[10] Clearly, another catalytic cycle is required, and there are two clues as to what

Scheme 7. Alternative Literature Mechanisms of Nitroxide Regeneration[a]



[a]Red color is used to indicate unfeasibly high activation barriers and highly endergonic reactions—factors which make these pathways improbable. Numbers in italics are calculated Gibbs free energies (kJ mol^{-1}, gas phase, 25 °C) of the reactions and activation (denoted by an asterisk).

this might be. First, results of isotopic labeling experiments using *N*-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidinyl benzoate in oxidizing cyclohexane at 60 °C[19] show unequivocally that (i) the cyclohexanone derived from this alkoxyamine acquires its oxygen atom exclusively from the alkoxyamine and (ii) the nitroxide derived from this alkoxyamine acquires its oxygen atom exclusively from the gaseous oxygen (as expected if an aminyl radical is formed in the recycling pathway). Second, Ananchenko and Fischer found that TEMPH was a product of the thermal decomposition of only those alkoxyamines that contained a *β*-hydrogen atom on the alkyl fragment, NOC*H*RR′.[22] Since the TEMPH-producing alkoxyamines have structures (Figure 3) that preclude N−OR homolysis, it is obvious that TEMPH formation must involve abstraction of their *β*-hydrogen atom. This reaction was also observed in laser flash photolysis experiments on the interactions between the alkoxyamines (structurally similar to those in Figure 3) and photosensitizers relevant to NMP.[62]

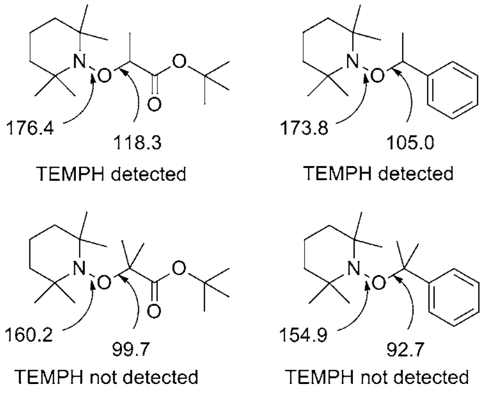
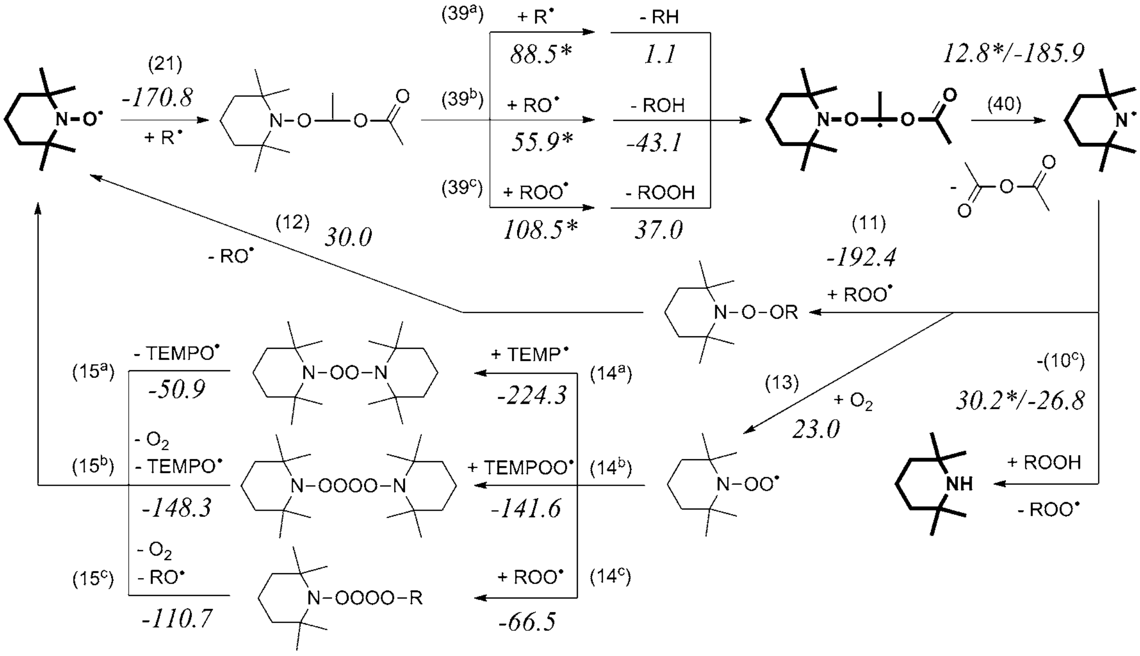


Figure 3. Alkoxyamines studied in ref 22 and corresponding calculated gas-phase Gibbs free energies (kJ mol^{-1}, 25 °C) of N−OR and NO−R bond homolysis.[11]

Our proposed catalytic cycle is summarized in Scheme 8 and involves an initial *β*-hydrogen atom abstraction from NOC*H*RR′ (via reactions 39^{a-c}). Of these reactions, abstraction by a peroxyl radical (reaction 39^{c}), although accompanied by the highest barrier, would be expected to dominate under most conditions of oxidative degradation because the steady-state concentration of peroxyls will be much higher than the steady-state concentrations of alkyls and alkoxyls. It should be noted that the proposed H-atom abstraction by a peroxyl radical,[16] from, e.g., TEMPOC*H*RR′ (R, R″ = alkyl) will be quite facile since it must be about as fast as H-atom abstraction from an isopropyl ether. The subsequent decomposition of the TEMPOC$^•$RR′ radical via *β*-scission (reaction 40) is strongly exoergic and provides the driving force for the process.[63] The resulting aminyl radical will then partition between regeneration of the nitroxide (reactions 11−15) and formation of amine (reverse of reaction 10^{c}). The overall process is strongly favored thermodynamically, and in contrast to all other possibilities examined, the barriers for each individual step leading to TEMP$^•$ are relatively modest, indicating that this process provides the most kinetically plausible mechanism for nitroxide cycling in these systems (see the normalized energy profiles in Figure S2 of the Supporting Information).

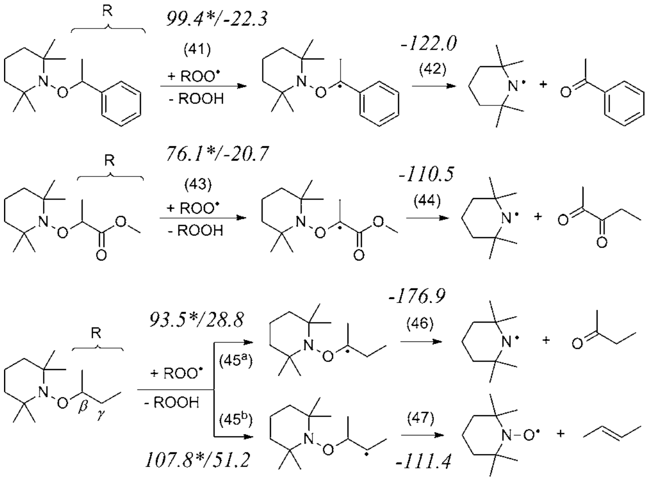
Scope and Applicability of the Proposed Catalytic Cycle. Although the calculations in this paper have largely focused on the kinetics and thermodynamics of various potential mechanisms for amine formation and nitroxide cycling in polyester degradation, we also evaluated key steps in our proposed mechanism for alkoxyamines that have been shown (theoretically[11] and experimentally[22,52]) to undergo predominantly NO−R bond homolysis. These include species expected to form in HALS-stabilized polystyrene, poly(methyl acrylate), and polyolefins (Scheme 9). For polyolefin-derived

Scheme 8. Proposed Cycle for Nitroxide Regeneration and Competitive Amine Formation via H-Atom Abstraction from an Alkoxyamine and Subsequent Aminyl Radical Formation[a]



[a] Numbers in italics are calculated Gibbs free energies (kJ mol^{-1}, gas phase, 25 °C) of the reactions and activation (denoted by an asterisk).

Scheme 9. Suggested Nitroxide Regeneration for Alkoxyamines Possessing a β-Hydrogen Atom[a]



[a]Numbers in italics are calculated Gibbs free energies (kJ mol^{-1}, gas phase, 25 °C) of the reactions and activation (denoted by an asterisk).

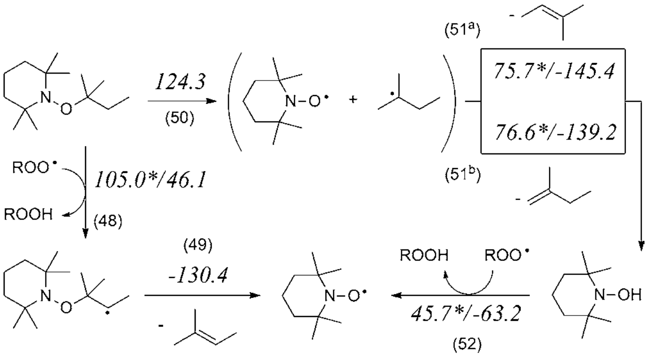
radicals, abstraction of a γ-hydrogen atom with the direct formation of a nitroxide is also considered (reactions 45^b and 47). With all of these alkoxyamines, the two crucial steps—H-abstraction yielding an alkoxyamine radical and its subsequent decomposition—are energetically feasible. Considering the two alternative H-abstractions for a model HALS–polyolefin system, abstraction from the β-position leading to TEMP$^\bullet$ is both kinetically and thermodynamically preferred over a γ-abstraction leading directly to TEMPO$^\bullet$. Thus, whereas the conventional JKZG catalytic cycle is only applicable to HALSs in which the OR group has an R which strengthens the NO–R bond, the mechanism suggested herein would appear to be perfectly feasible for other types of polymer-derived alkoxyamines provided they possess a β-hydrogen atom, OC*H*RR′.

HALSs are known to be less effective in polymers for which the degrading radicals captured by TEMPO$^\bullet$ are tertiary and so do not contain a β-hydrogen atom, e.g., polypropylene.[17] In photo-oxidized polypropylene it is assumed that inactive *tert*-alkoxyamines accumulate,[16,46] whereas under thermal degradation these alkoxyamines can effectively regenerate nitroxides.[16] In polypropylene the nitroxides are not able to cycle by the proposed β-hydrogen abstraction so that any cycling that does occur presumably involves one, or more, of the energetically less favored pathways described above. Many of these paths were considered in our earlier study of the Denisov cycle,[21] but they generally involved enormous activation barriers. A more energetically feasible cycle, discussed in the present study, involves H-atom abstraction from the γ-position, followed by the formation of TEMPO$^\bullet$ and alkene (Scheme 9). At higher temperatures, NO–R bond cleavage will be facilitated and the resultant nitroxide could re-enter the BBF cycle (reactions 35 and 36 in Scheme 7). Such a mechanistic pathway is considered for a model tertiary alkyl radical in Scheme 10, and the results indicate that these processes are likely to contribute significantly to the stabilizing action of HALSs in thermally degrading polypropylene and analogous polymers.

■ CONCLUSIONS

In contrast to phenolic RTAs, amine RTAs are active at high temperatures and frequently exhibit very high inhibition stoichiometric factors, which makes them highly effective antioxidants for lube oils and plastics over a wide range of operating conditions. The origin of their high stoichiometric factors has long been debated, with several mechanisms and side reactions having been proposed. On the basis of the evidence presented above, the vast majority of these mechanisms can be discounted on kinetic or thermodynamic grounds. We conclude, nevertheless, that a number of different activation mechanisms and regeneration cycles are likely to be involved depending on the external conditions (temperature, UV light, etc.) and the chemical nature of both the degrading substrate and the stabilizer employed.

Scheme 10. Alternative Nitroxide Regeneration Pathways for the Alkoxyamines Lacking a β-Hydrogen Atom[a]



[a]Numbers in italics are calculated Gibbs free energies (kJ mol^{-1}, gas phase, 25 °C) of the reactions and activation (denoted by an asterisk).

- The activation of the initial HALSs depends on their chemical functionality. For secondary amines, we have confirmed the literature proposals[17,47] that they are first converted to aminyl radicals through a hydrogen abstraction and then oxidized to nitroxides either via formation and subsequent decomposition of an *O*-alkylperoxyamine or by addition of O_2 followed by coupling with another radical and subsequent decomposition (reactions 10–15 in Scheme 4). For (tertiary) *N*-methyl-HALSs, our new activation mechanism (reactions 16–20 in Scheme 4) involves H-abstraction from the *N*-methyl group and subsequent addition of oxygen to form the corresponding peroxyl radical, followed by reactions yielding the alkoxyl radical TEMP-CH$_2$O$^\bullet$, the β-scission of which yields the aminyl radical and hence the nitroxide.
- Diarylamines owe their catalytic activity to a cycle known as the *JKZG cycle* (Scheme 2), which occurs because of the stabilization provided to an intermediate aminyl radical by the aromatic substituents. Since this stabilization is not present in dialkylamine RTAs (including dialkylamine-based HALSs), these species can only follow this catalytic cycle when the oxidizing substrate yields R$^\bullet$ radicals that promote N–OR homolysis of the intermediate alkoxyamines.[53] Even in these special cases, this route is generally less energetically favorable for dialkylamine RTAs than our new catalytic cycle (Scheme 8).
- We attribute the antioxidant activities of most commercial HALSs to a *new catalytic cycle* (Scheme 8) in which the β-hydrogen atom in the alkoxyamine is abstracted by a peroxyl radical with the subsequent

formation of a ketone and an aminyl radical. This mechanism not only is kinetically preferred according to our high-level ab initio calculations, but also explains key experimental observations—the selective formation of secondary amines at high temperatures in substrates that would yield alkoxyamines with a β-hydrogen, the exclusive formation of ketone containing the oxygen atom of the alkoxyamine, and the exclusive formation of nitroxide containing an oxygen atom derived from dioxygen.

- Finally, if the alkoxyamine does not have a β-hydrogen, high stoichiometric factors may still occur because of the *abstraction of a γ-hydrogen* or by entry into the *BBF cycle* (Scheme 10). These processes are not as energetically favorable as either of the other two cycles, which explains why HALSs are generally less effective antioxidants for such substrates.

In this paper we have addressed a significant gap in the complex and multifaceted chemistry of dialkylamine radical-trapping antioxidants. The β-hydrogen abstraction from alkoxyamines that has been proposed also seems likely to play some role in other applications of nitroxides such as their use as radical traps and as control agents in nitroxide-mediated polymerization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete refs 27 and 28, additional assessment of computational procedures, normalized energy profiles of studied processes, detailed discussions of improbable pathways, additional schemes and calculations, calculated thermodynamic and kinetic parameters of investigated reactions in the gas and solution phases, optimized geometries in the form of Gaussian archive entries, and corresponding total energies, thermal corrections, zero-point vibrational energies, entropies, free energies, and free energies of solvation for all species in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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