Mechanistic Insights into N-Acyloxyamine-Initiated Controlled Degradation of Polypropylene: The Unexpected Role of Keto-Enol Tautomerization in Carboxylate Radical Chemistry

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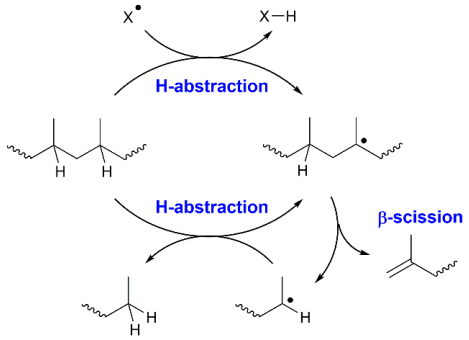
ABSTRACT: Controlled degradation of polypropylene (PP) is used industrially to improve the properties of crude PP. While traditionally initiated by organic peroxides, N-acyloxyamines are now preferred due to their greater stability. However, their mechanism of action remains unclear. Using high level ab initio calculations, we show that N-O homolysis is the most likely fragmentation pathway available to N-acyloxyamines, in contrast to the more usual C-O homolysis observed for the closely related N-alkoxyamines. This would, in theory, generate aminyl and carboxylate radicals, with the latter undergoing decarboxylation to generate methyl radicals. However, the enol-form of N-acyloxyamines is significantly less thermally stable, having bond dissociation free energies that are over 50 kJ/mol below that of their keto equivalent. Under conditions where keto-enol tautomerism is feasible, enol N-O homolysis, which forms the more stable acetic acid radical, would be the dominant degradation pathway. This reveals the crucial and underappreciated role that polar impurities play in the initiation process of enolizable initiators and may explain contradictory observations in the experimental literature. The product aminyl radicals are susceptible to β-fragmentation, releasing alkyl radicals and affording imines, which in turn are susceptible to allylic H-abstraction and further β-fragmentation leading to dialkyl pyridines as the ultimate degradation products.

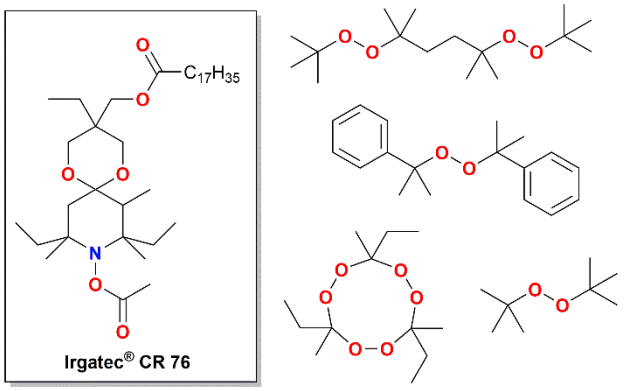
INTRODUCTION

Polypropylene (PP) is a commodity thermoplastic polymer used in a wide variety of consumer products, ranging from textiles and packaging to appliance casing and plumbing.[1] By volume, PP is the second-most commonly produced commodity plastic (after polyethylene). It is typically produced via chain-growth polymerization employing coordination (Ziegler-Natta) catalyst systems,[1] with the crude polymer usually having a relatively high molecular weight and a large dispersity (Đ).[2-4] For many end-use applications, crude PP possesses unsuitable physical and chemical properties; for instance poor melt flow and extrusion characteristics.[3] However, these properties are dependent on the polymers molecular weight distribution, specifically the number averaged and weight averaged molecular weight (M_n and M_w, respectively) and Đ value.[5, 6] Subjecting this crude material to controlled radical degradation can dramatically alter its molecular weight distribution and enhance its mechanical properties.[7] This degradation results in chain-scission, which reduces molecular weight and improves the polymers processability (see **Scheme 1**). Mechanistic aspects of this process (in the presence of peroxide initiators) was previously examined by Marque and co-workers.[8]



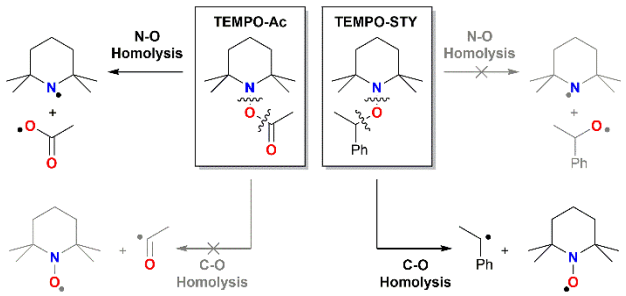
Scheme 1. The controlled degradation of polypropylene (PP) via H-abstraction followed by β-scission.

Approximately 20 years ago, Ciba SC discovered that N-acyloxyamines behave as powerful initiators of radical polymerization and degradation.[9] Following this discovery, several patent applications claiming the use of these novel radical initiators for grafting of ethylenically unsaturated carboxylic acid derivatives onto thermoplastic polymers,[10] curing of photoresists compositions,[11] curing of coatings,[12] or use as flame retardants[13] were then filed. Arguably the most important industrial application of this class of initiators is for controlled degradation of polypropylene (PP).[14] For this application, a tailor-made compound has been developed and commercialized under the trade name Irgatec® CR 76 (see **Scheme 2**),[15] which is used as a safe, non-explosive alternative to the explosive and fire supporting peroxides normally used for controlled degradation processing.



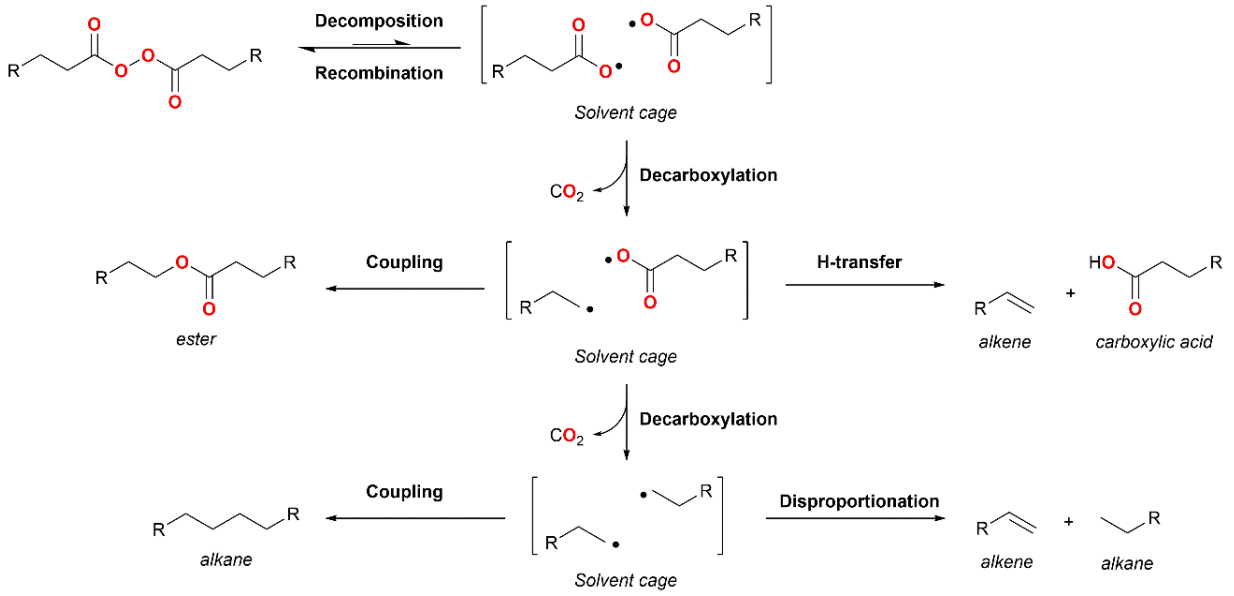
Scheme 2. Irgatec® CR 76 and various peroxides used for controlled degradation of polypropylene. Note that Irgatec® CR 76 is a mixture of stereoisomers.

The actual mechanism by which N-acyloxyamines work as radical initiators is not well understood. Density Functional Theory (DFT) calculations by Tidwell and co-workers[16] as well as Gigmes and co-workers[17] suggest that they should undergo homolysis along their N-O bond to afford transient aminyl radicals and carboxyl radicals (see **Scheme 3, left**). Indeed, in the present study, this mode of cleavage will be demonstrated using high-level composite calculations (vide infra). These transient radicals (or their transformation products) should be able to initiate controlled degradation. This mode of cleavage contrasts with that of the closely related N-alkoxyamines, such as TEMPO-STY, which are well known for undergoing C-O fragmentation provided the leaving R group is sufficiently stabilizing (see **Scheme 3, right**).[18, 19] During Nitroxide Mediated Polymerization (NMP), N-alkoxyamines undergo reversible homolysis of their weak C-O bond affording persistent nitroxide radicals and transient propagating radicals.[20, 21]



Scheme 3. N-O vs C-O cleavage in a prototypical N-acyloxyamine (TEMPO-Ac) and an N-alkoxyamine (TEMPO-STY).

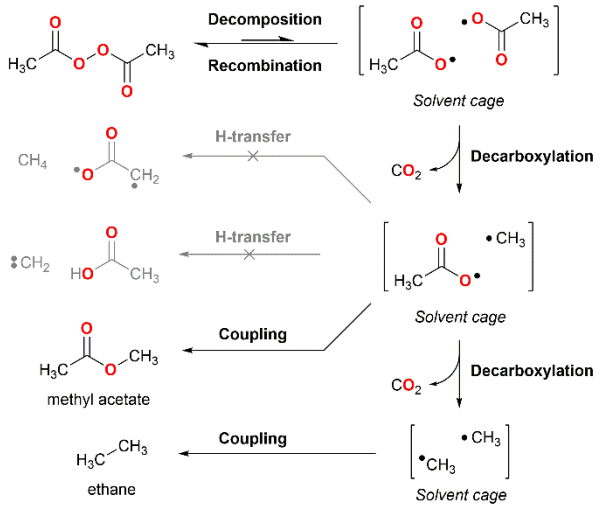
Gigmes and co-workers proposed that direct N-O homolysis forming carboxylate radicals operates during pyrolysis of N-acetyloxy phthalimide.[17] However, carboxylate radical reactivity itself has been the subject of enormous literature controversy, with conflicting reports centered around the observation of different decomposition products. Initial reports suggested that carboxylate radicals (formed via O-O homolysis of diacyl peroxides) undergo essentially spontaneous decarboxylation and were thus utilized as sources of primary alkyl radicals.[22-25] Indeed, Ryzhkov and co-workers found that typical carboxylate radicals undergo ultrafast decarboxylation, with rate coefficients, $k > 10^9$ s^{-1} at 80 °C.[26] Ryzhkov and co-workers[26] noted that the diacyl peroxide decomposition process yields significant quantities of ester, carboxylic acid,



Scheme 4. Potential cage reactions of a symmetric diacyl peroxide initiator bearing α and β CH_2 groups.

alkanes and alkenes (in addition to other minor) products (see **Scheme 4**). Similar species were identified by Gilmer and co-workers, in their earlier study of diacyl peroxide decomposition.[27] While the precise ratio of decomposition products is highly sensitive to the identity and concentration of the diacyl peroxide (as well as temperature and solvent), it is generally thought to be indicative of rapid decarboxylation and mostly (or solely) in cage reactivity.[26, 27] In the case of diacyl peroxides lacking β hydrogen atoms, such as diacetyl peroxide, cage-based H-transfer pathways would be suppressed and far fewer cage decomposition products would be anticipated (see **Scheme 5**). As such, cage reactions would afford predominantly ethane and methyl acetate. Indeed, Martin and co-workers used isotopic ^{2}H and ^{18}O labelling to establish that the ethane and methyl acetate formed via diacetyl peroxide decomposition result from in-cage reactions.[25]

In contrast to these reports, successful radical reactivity has been noted during diacetyl peroxide decomposition.[23, 28, 29] For instance, Gladstone and co-workers noted that in solutions of acetic and isobutyric acid, diacetyl peroxide decomposition affords significant quantities of succinic and tetramethyl succinic acid, respectively.[29] The presence of these dicarboxylic acid products is indicative of cage escape of the initially formed (diacetyl peroxide derived) radicals, followed by solvent mediated H-abstraction and then radical coupling.[29] Similarly, Drew and co-workers noted that carboxylate radicals derived from diacetyl peroxide could be added across the C=C bond of cyclohexene.[23] Using galvinoxyl as a radical scavenger, these authors firmly established that the formation of cyclohexyl acetate and 3-cyclohexenyl acetate occurred via addition of carboxylate radicals that had escaped from the solvent cage (without undergoing decarboxylation).[23] Perhaps most significantly, May and co-workers observed that an array of simple alkyl carboxylate radicals undergo H-abstraction at low temperature.[28] Generating acetoxy, propionoxy, isobutyroxy and pivaloxy radicals via acyl hypobromites (RCO_2Br), May established that radical brominations of alkanes and haloalkanes occurred with satisfactory yields.[28] Moreover, no significant differences in yield or selectivity were observed as the R group was varied, which is indicative of an $RCO_2^{\bullet}$ mediated reaction and somewhat incompatible with an alkyl radical ($R^{\bullet}$) mediated process.[28]



Scheme 5. Potential cage reactions of diacetyl peroxide. Disproportionation and H-transfer between the transient methyl and acetate radicals and would afford either a carbene ($:CH_2$) or acetoxyl diradical, neither of which would be thermodynamically and/or kinetically favorable.

Clearly, rapid decarboxylation of carboxylate radicals is at odds with reports of their alkene addition products. Moreover, reports of diacyl peroxide decomposition affording predominantly (non-radical) cage products is in clear contrast to reports of successful mediation of radical-based bromination and coupling reactions. May and co-workers attempted to reconcile these divergent observations by suggesting that carboxylate radicals could be generated in two different electronic states (denoted π and σ) and hypothesizing that these states possessed differing reactivities.[28, 30] While the presence of low lying excited states was later confirmed with photoelectron spectroscopy and ab initio calculations,[31] it remains unclear if this near degeneracy provides an adequate explanation for the apparently divergent reactivity of carboxylate radicals.

Given their success in initiating controlled PP degradation, the decomposition products of Irgatec® CR 76 (and other N-acyloxyamines) are clearly successfully abstracting H-atoms from PP polymer as depicted in **Scheme 1**. Intriguingly, in unpublished studies, we have observed nearly stoichiometric amounts of acetic when various N-acyloxyamines were decomposed in the presence of PP. Similarly, Gigmes and co-workers recently reported near stoichiometric acetic acid generation when N-acetyloxy phthalimide, which is also thought undergo N-O homolysis,[17] was utilized for polyethylene grafting and functionalization.[32] These results are clearly indicative of successful escape of the caged carboxylate radical with little if any decarboxylation.

Moreover, the precise fate of the aminyl radical fragment and its role in the controlled degradation process is also unclear. In model studies of the alkoxyamines relevant to the chemistry of hindered amine light stabilizers (HALS) and NMP, it has been shown that aminyl radicals are capable of hydrogen abstraction to produce secondary amines.[33, 34] Moreover, production of aminyl radicals has been shown to be an important step in the cycle by which HALS protect polymers *from* degradation.[35] However, oxygen plays a crucial role in the normal operation of the HALS mechanism, oxidizing the relatively reactive aminyl radicals into persistent nitroxides that can couple with reactive polymeric radicals (facilitating their deactivation).[35] As oxygen is normally excluded during controlled PP degradation, the role and fate of aminyl radicals is unclear.

Given the numerous important industrial applications of these species, the mechanistic understanding of N-acyloxyamine (and diacyl peroxide) chemistry is clearly lacking. As rational design hinges on a detailed mechanistic understanding of the process of interest, resolving these apparent discrepancies would be of significant interest. In this work, we used high-level theoretical calculations to study N-acyloxamine and diacyl peroxide decomposition in the context of controlled PP degradation.

COMPUTATIONAL PROCEDURES

All standard *ab initio* molecular orbital theory and density functional theory (DFT) calculations were carried out using Gaussian 09[36] and Molpro[37] software packages. Procedures were chosen based on benchmarking against experiment in previous studies of similar systems.[38, 39] Geometries were optimized at the M06-2X/6-31+G(d,p)[40] level of theory, and frequencies were also calculated at this level. Single point energies were calculated using the high-level composite *ab initio* method G3(MP2)RAD [41] and G3(MP2)RAD(+). G3(MP2)RAD(+) is a variant of standard G3(MP2)RAD[41] where the calculations with the 6-31G(d) basis set are replaced with corresponding 6-31+G(d) calculations to allow for better treatment of anionic species. These high-level calculations were utilized in conjunction with the ONIOM style approximation for larger systems,[42, 43] where the full system was modelled using ROMP2/GTMP2Large//M06-2X/6-31+G(d,p). Gibbs free energies in the gas-phase were calculated using standard ideal gas partition functions, under the harmonic oscillator/rigid rotor approximation. Gibbs free energies in solution were calculated via a thermocycle in which Gibbs free energies in the gas-phase were combined with Gibbs free energies of solvation and the necessary phase change correction term.[44] The SMD solvent model[45] was used to correct for implicit solvent effects in water and dimethyl sulfoxide (DMSO). For this purpose, geometries were fully optimized in solution at the M06-2X/6-31+G(d,p) level.

RESULTS AND DISCUSSION

Decarboxylation and H-transfer of Carboxylate Radicals As literature on the reactivity of carboxylate radicals is seemingly contradictory, we employed high-level theoretical calculations to study these reactions from first principles. As anticipated, the decarboxylation of an isolated acetate radical, $CH_3COO^{\bullet}$, is predicted to be very rapid, even at room temperature, with a $\Delta H^{\ddagger}$ of only 5.4 kJ/mol and $\Delta G^{\ddagger}$ of 8.7 kJ/mol (see **Figure 1**). Unsurprisingly, decarboxylation is also predicted to be a strongly exergonic across the temperatures studied. The predicted $\Delta G^{\ddagger}$ and corresponding fragmentation rate coefficients, as well as ΔG_{rxn} values, at 200 °C, 250 °C and 300 °C are listed in **Table 1**. As decarboxylation is a unimolecular reaction, the rate coefficient will not be limited by bimolecular diffusion. Importantly, these predicted rate coefficients are still slower than the limiting timescale for molecular vibrations (~ 10^{-14} s for a bond-stretch) and are thus meaningful.

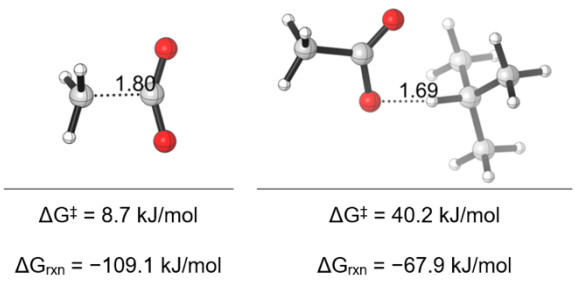


Figure 1. A comparison of the kinetics and thermodynamics of decarboxylation vs H-atom transfer. The fragmenting C-C bond (left) and forming O-H bond (right) distances are given in Å.

For comparison, the barriers and corresponding rate coefficients for H-transfer between this O-based carboxylate radical and a unimeric polypropylene model, $HC(CH_3)_3$, are given in **Table 1**. We should caution that these predicted rate coefficients do not include tunneling corrections. However, given the very small enthalpic barriers observed here and the high temperature of typical PP degradation conditions, tunneling corrections are probably not significant. Indeed, the rate coefficient for this H-transfer process is probably approaching the diffusion limit, which is typically on the order of 10^7 $M^{-1}s^{-1}$ for low viscosity solvents. Unfortunately, it is somewhat unclear what diffusion value might be applicable in the context of PP degradation, but the solution value would provide an upper bound. Hence, these calculations confirm that bimolecular H-transfer between isolated acetate radicals and PP would be uncompetitive compared with unimolecular decarboxylation. To account for the formation of acetic acid via normal N-O homolysis, the resulting carboxylate radicals would therefore have to undergo extremely rapid in-cage H-transfer.

Table 1. Gibbs Free Energies[a] of activation and reaction for decarboxylation vs H-transfer of $CH_3COO^{\bullet}$ radical in the gas-phase.

Temp (°C)	Decarboxylation			H-transfer		
	ΔG‡	k (s^{-1})	ΔG_{rxn}	ΔG‡	k ($M^{-1}s^{-1}$)	ΔG_{rxn}
200	10.6	6.6×10^{11}	-127.8	64.1	3.2×10^{7}	-70.0
250	11.2	8.2×10^{11}	-133.1	70.9	3.9×10^{7}	-70.7
300	11.8	1.0×10^{12}	-138.5	77.5	4.8×10^{7}	-71.4

[a]Values given in kJ/mol.

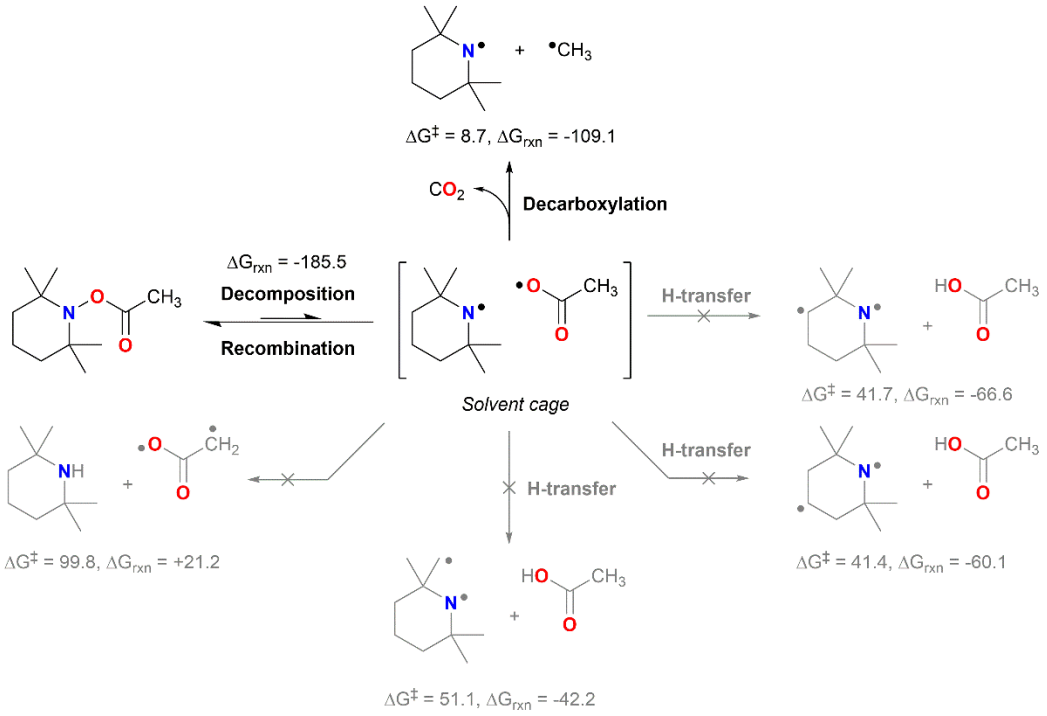


Figure 2. A comparison of hypothetical cage reactions available to the aminyl and carboxylate radical. Thermodynamics and kinetics for decarboxylation and radical-radical coupling were calculated at the G3(MP2)RAD//M06-2X/6-31+G(d,p) level of theory. Thermodynamics and kinetics for the H-transfer reactions were calculated with M06-2X/6-31+G(d,p), with all diradical species modelled in their triplet configurations. All values given in kJ/mol and calculated a 25 °C.

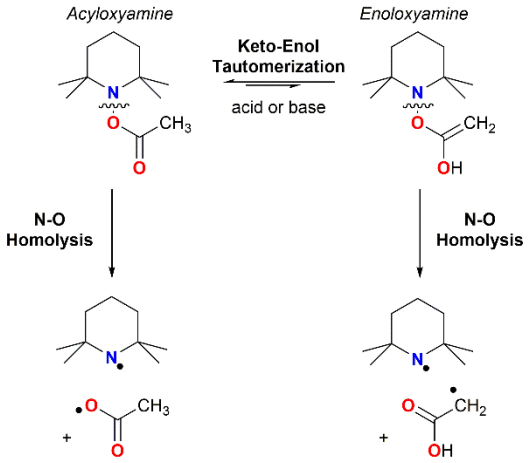
N-O and C-O cleavage in N-acyloxyamines To confirm that the preferred mode of thermal fragmentation of N-acyloxamine is via N-O cleavage, we investigated the principle fragmentation products of

TEMPO-Ac. The predicted Bond Dissociation Enthalpy (BDE) for the N-O bond is 250.0 kJ/mol vs 268.1 kJ/mol for C-O cleavage (see **Figure 2**). Interestingly, N-O fragmentation is also more entropically favorable than C-O cleavage; with a predicted Bond Dissociation Free Energy (BDFE) of 185.5 kJ/mol compared with 209.8 kJ/mol (at room temperature).

This difference was found to originate from both the vibrational and external rotational component of the entropy. Obviously, as temperature increases, the BDFE for N-O cleavage is lowered faster than C-O cleavage; with predicted BDFEs at 300 °C of 126.1 kJ/mol and 156.4 kJ/mol, respectively. As both N-O and C-O homolysis of alkoxyamines is barrierless on the enthalpic surface,[21] these calculations indicate that N-O cleavage would be the predominant thermal fragmentation pathway. Hence N-acyloxyamines have similar homolytic behavior to the closely related N-acyloxy phthalimides; with the corresponding acetyloxy phthalimide possessing N-O and C-O BDFEs of 178.2 and 217.4 kJ/mol at 300 °C, respectively (See Table S2 in the Electronic Supporting Information).

To exclude the possibility of in cage reactivity as a potential route to radical initiation and acetic acid generation, we investigated potential in-cage H-transfer reactions of TEMPO-Ac (see **Figure 2**). Like diacetyl peroxide, TEMPO-Ac lacks β-H atoms on either of the radicals generated from N-O homolysis. Hence, in-cage H-transfer cannot afford non-radical products and instead various alkyl-aminyl (and acetoxyl diradical) diradicals would be generated. As Figure 2 indicates, none of these in cage H-transfer reactions are predicted to be competitive with decarboxylation. Of the various in-cage H-transfer products, the cyclic 1,3 and 1,4 alkyl-aminyl diradicals are the most kinetically and thermodynamically favorable. However, even the fastest in cage H-transfer reaction is significantly slower than radical (re)coupling and decarboxylation.

Keto-enol Tautomerism in N-acyloxyamines, diacyl peroxides and N-acyloxy phthalimides Enolization refers to the conversion of carbonyl species (in the presence of an acid or base catalyst) into an enol. In previous calculations, we have assumed that the N-acyloxyamine, TEMPO-Ac, predominantly exists in its keto tautomer. However, the enol tautomer of N-acyloxyamines is of interest because N-O fragmentation of the enol form of TEMPO-Ac intrinsically bypasses the formation of the O-based acetate radicals in favor of the C-based acetic acid radical, $^{\bullet}CH_2COOH$ (see **Scheme 6**). These carboxylic acid radicals could then initiate PP degradation via H-abstraction, explaining the generation of near stoichiometric quantities of acetic acid.



Scheme 6. Keto-enol tautomerism of TEMPO-Ac. The enol radical is depicted in its major (C radical) resonance contributor.

TEMPO-Ac has been synthesized and characterized by several different research groups, with characterization indicating no detectable enolization under standard conditions. Consistent with these reports, the enol tautomer of TEMPO-Ac is unstable relative to the keto species by 87.5 kJ/mol enthalpically and 92.9 kJ/mol in Gibbs Free Energy (at room temperature, see **Figure 3**). As the Gibbs Free Energy difference between the keto and enol species is nearly entirely enthalpically based, the respective ΔG is not significantly affected by temperature; increasing only slightly to 97.3 kJ/mol at 300 °C. This suggests that under standard conditions and even at elevated temperatures, the transient enol concentration would be essentially negligible and enol formation would likely be undetectable by direct experimental characterization procedures. However using lithium diisopropylamide (LDA) as a base, Inokuchi and co-workers reported the generation of the Li-enolates of various N-acyloxyamines (including TEMPO-Ac) and demonstrated the synthetic utility of these transient species for low temperature (–78 °C to 6 °C) nucleophilic C2 alkylation reactions.[46]

As the Curtin-Hammett principle states, the relative concentration of two interconvertible substrates does not influence the product composition.[47] Instead, the product ratio is only controlled by the relative Gibbs Free Energies of the respective transition sates ($\Delta\Delta G^{\ddagger}$).[47] In this context, the Curtin-Hammett principle mandates that the ratio of keto and enol tautomers does not predict the preferred fragmentation pathway, which is instead determined by the relative decomposition barrier heights (and hence BDFEs as reverse reaction is essentially barrierless[21]) of the two pathways provided keto-enol tautomerism itself is rapid. Both N-O fragmentation pathways form the aminyl radical, with the only difference being the enol pathway forms the acetic acid radical ($^{\bullet}CH_2COOH$) instead of the acetate radical ($CH_3COO^{\bullet}$). We should emphasize the relevance

of enolization hinges on the precise conditions employed, as keto-enol tautomerization requires the presence of acidic or basic catalysts.

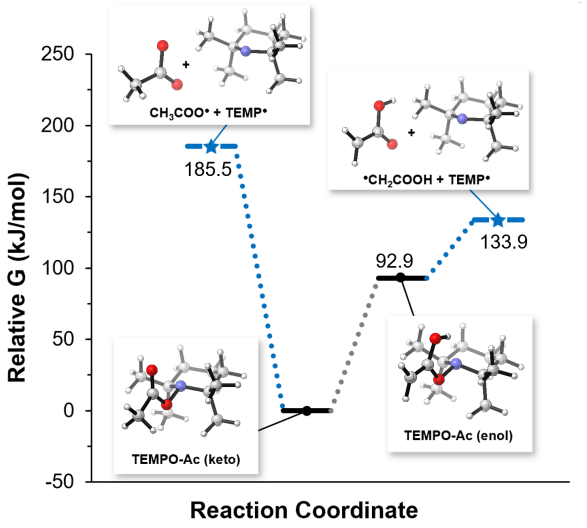
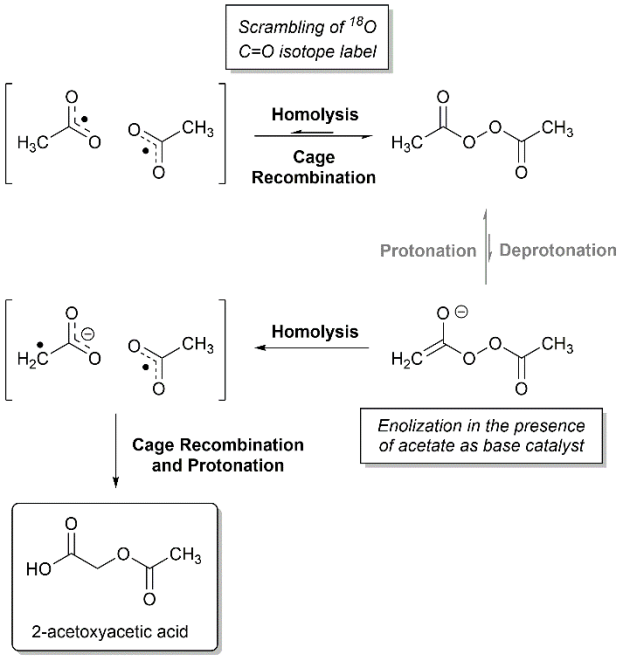


Figure 3. The Structures and relative Gibbs Free Energies at 25 °C of the keto and enol forms of TEMPO-Ac and the respective N-O cleavage products.

Various experimental studies unambiguously confirm that this acetic acid radical is substantially more stable than the acetate radical, with respective C-H and O-H BDEs of approximately 400 and 445 kJ/mol, respectively.[48] Indeed, our high-level calculations suggest reasonably comparable BDE values of 410 and 470 kJ/mol for the C-H and O-H bonds in acetic acid. Thus, provided the keto and enol species can tautomerize, enol fragmentation would be the dominant homolysis pathway. Specifically, enol-fragmentation is favored by 51.5 kJ/mol in terms of BDFE over the keto-fragmentation (at room temperature, see **Figure 3**). This preference persists at higher temperatures, with a predicted ΔBDFE of 45.3 kJ/mol at 300 °C in favor of the enol pathway.

The finding that enolization can significantly lower the effective BDFE of TEMPO-Ac is intriguing. Moreover, because the BDFE lowering upon enolization originates from the underlying stability difference between the $^{\bullet}CH_2COOH$ and $CH_3COO^{\bullet}$ radicals, it is also transferable to other acetyl containing initiators. As such, comparable Gibs Free energy diagrams are observed with diacetyl peroxide and N-acetyloxy phthalimide (See Figure S1 and S2 in the Electronic Supporting Information). Because of this transferability, we wondered if similar results had been reported previously (but not widely appreciated) and if some of the inconsistencies regarding carboxylate radical decomposition could be attributed in part to enolization mediated decomposition.

For diacyl peroxides, partial enolization followed by O-O homolysis and in cage recombination of the product radicals should afford ester-substituted carboxylic acids (or their conjugate bases), which would be stable and inactive as radical initiators (see **Scheme 7**). Pleasingly, Wielesek and co-workers actually reported conclusive evidence for enolization in acetyl peroxide decomposition around 50 years ago.[49] These authors found that acetyl peroxide readily reacts, in the presence of acetate salts at room temperature, to afford 2-acetoxyacetic acid.[49]



Scheme 7. Enolization of diacetyl peroxide and cage recombination to form thermally stable 2-acetoxyacetic acid. O-O homolysis of the keto tautomer results in detectable scrambling of ^{18}O carbonyl labels.

Unsurprisingly, this reaction was inhibited by the neutralization of acetate with added acetic acid. Using ^{14}C acetate labelling, these authors did note some incorporation of the acetate base into the product acetoxyacetic acid, which could occur via several different radical and non-radical pathways.[49] However, they found that 55-70% of this product was not isotopically labelled, suggesting that the acetate could also simply act as a base catalyst.[49] These observations are entirely consistent with an enolization mediated decomposition mechanism. As Figure S1 in the supporting information indicates, the enol tautomer of the acetyl peroxide is unstable relative to its fragmentation products on the Gibbs Free Energy Surface. Indeed, the O-O BDFE of the intermediate acetyl peroxide enolate is around 8.7 kJ/mol in the gas-phase. This suggests that the homolysis of diacetyl peroxide likely occurs directly via its enolate to afford the $^{\bullet}CH_2COO^{-}$ radical-anion (see Scheme 7) rather than

occurring via the enol tautomer. However, for the purposes of the present work, we simply note that the effective BDFE of diacetyl peroxide should be substantially lowered in the presence of base catalyst; with both the intermediate enolate and enol tautomer offering more thermodynamically viable fragmentation pathways than the keto tautomer.

pK_a values of N-acyloxyamines, Diacyl peroxides and N-acyloxy phthalimides. Based on the above results, it appears that some of the previous confusion in the literature regarding the lifetime of carboxylate radicals, may be explainable in terms of decomposition proceeding via enolization. As keto-enol tautomerization is usually prohibitively slow in the absence of polar impurities, enol mediated decomposition would not be kinetically viable in strictly non-polar environments. Under such conditions, the effective BDFE should reflect keto tautomer decomposition and greater thermal stability would be expected. Indeed, many experimental studies that have examined the kinetics of diacyl peroxide decomposition have done so in meticulously purified non-polar solvents. Under such conditions, little if any enolization would be anticipated. However, if polar impurities are present, the effective BDFE would become increasing reflective of enol tautomer decomposition and so significantly lower thermal stability would be observed.

The kinetics of keto-enol tautomerism are heavily dependent on the solvent environment; particularly, the identity and concentration of polar impurities. As such, it is somewhat difficult to precisely confirm when this enolization becomes significant. Moreover, in many cases the keto decomposition products may be sufficiently polar to catalyze keto-enol tautomerism (ultimately leading to autocatalytic degradation). To demonstrate the general thermodynamic feasibility of base-catalyzed enolization, we calculated energetics for enolization of diacetyl peroxide and TEMPO-Ac using acetate as a prototypical base. We also calculated the relative pK_a values of these two initiators in different solvents, using acetone used as a reference acid.[50, 51]

As Table 2 illustrates, even relatively modest bases such as acetate can appreciably catalyze keto-enol tautomerization. While proton exchange between acetate and diacetyl peroxide or TEMPO-Ac is reasonably endergonic (as reflected by the appreciable pK_a difference), the intermediate enolate is still notably more stable than the keto decomposition products. In other words, although base-catalyzed enolization proceeds via relatively high energy intermediate enolates, it still offers a more kinetically and thermodynamically favorable decomposition pathway than standard homolysis of the keto tautomer of the initiator.

Table 2. Gibbs Free Energies[a] for gas-phase enolization of diacetyl peroxide, TEMPO-Ac and N-acetyloxy phthalimide using acetate as a prototypical base. pK_a values in different solvents are also given.

Species	$\Delta G_{enolate}$	pK_a	
	Gas	DMSO	water
Diacetyl Peroxide	+47.9	25.1	19.8
TEMPO-Ac	+86.3	28.7	22.2
N-acetyloxy phthalimide	+39.1	21.5	15.9
Acetic acid	-	12.6[b]	4.8[b]

[a]Values given in kJ/mol. [b]Taken from reference [52, 53]

In the context of controlled PP degradation, we note that an array of polar compounds, including phenolic stabilizers and calcium stearate (which is used as a lubricant and release agent) are employed as additives in PP resins. Given the inherent polar functionality of N-acyloxyamines themselves, it is highly likely that their local chemical environment within a PP resin would encompass sufficiently polar species to enable keto-enol tautomerism. Thus, enol mediated decomposition nicely accounts for the generation of near stoichiometric quantities of acetic acid upon N-acyloxyamine decomposition.

Fate of the aminyl radical. The role and fate of the aminyl radical is another significant question regarding the mechanism of N-acyloxyamine initiated controlled PP degradation. A prototypical tetramethyl piperidine aminyl radical can undergo β-fragmentation with a modest barrier (c.a. 100 kJ/mol at 25 °C, blue pathway) to generate a methyl radical and a 2,2,6-trimethyl imine. The reaction energy for this process is essentially thermoneutral at room temperature but becomes increasingly favorable as temperature is increased (e.g. 200 °C, red pathway). The 2,2,6-trimethyl iminyl radical can undergo another β-fragmentation to eliminate a methyl radical, although a more significant barrier (c.a. 150 kJ/mol) is observed, regardless of temperature. However, the thermodynamic favorability of this elimination to generate the 2,6-dimethyldihydropyridine is clearly influenced by temperature. The 2,6-dimethyldihydropyridine would be highly susceptible to further radical degradation, for instance via double H-abstraction, to generate 2,6-lutidine.

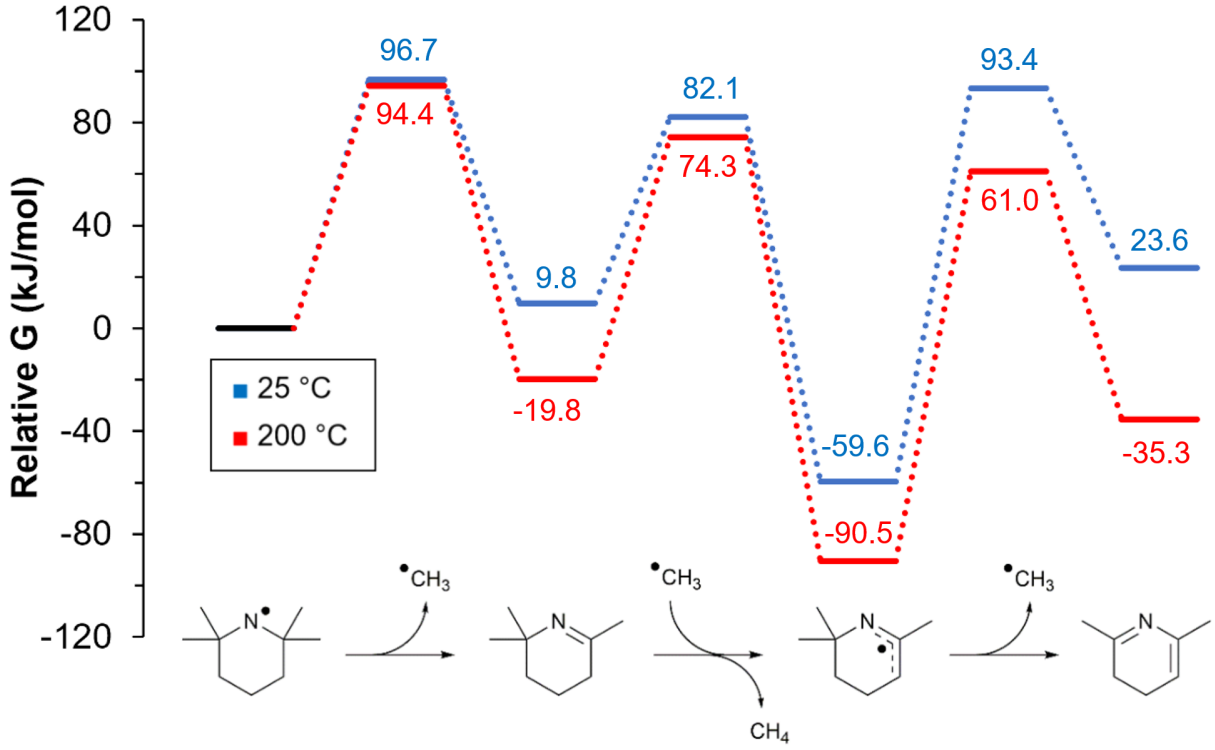


Figure 4. A possible degradation pathway of a tetramethyl piperidine aminyl radical. Initial β fragmentation affords an imine and $^{\bullet}CH_3$ radical, with subsequent H-transfer affording an iminyl radical. Futher β fragmentation affords 2,6-dimethyldihydropyridine.

Interestingly, the barrier of both β-fragmentations appear to be largely temperature independent, with the relatively localized aminyl radical undergoing much faster β-fragmentation than the delocalized iminyl radical. Thermodynamically, elimination is slightly more favorable from aminyl radical than the iminyl radical, which can be rationalized in terms of radical stability of the reagent radicals. However, the reaction energy of both β-fragmentations is very temperature dependent; with thermodynamic favorability increasing at higher temperatures due to entropic factors (see Figure S3, Supporting Information). The barrier for H-abstraction increases somewhat with temperature due to entropy, but the thermodynamics of this process are reasonably temperature independent. While the $^{\bullet}CH_3$ radicals produced via the β-scission reactions are more reactive, favorable kinetics and thermodynamics are still observed with a $^{\bullet}CMe_3$ radical (as a model for PP derived radicals). Finally, the 2,6-diethyl-2,3,6-trimethylpiperidine aminyl radical was considered as a model for the aminyl radical generated from Irgatec® CR 76. Its fragmentation pathways shown in Figure S3 of the Supporting Information suggest that cleavage of $^{\bullet}CH_2CH_3$ radicals rather than of $^{\bullet}CH_3$ radicals will be preferred in its β-fragmentations.

CONCLUSION

Summing up, acyloxyamines initiate controlled radical degradation via N-O homolysis. However, in contrast to conventional wisdom it is the enol form that undergoes cleavage to produce an acetic acid radical, hence explaining the stoichiometric production of acetic in such systems. The keto-enol tautomerization is initially catalyzed by polar impurities, which play a key under-appreciated role in this process; the acetic produce then makes this process autocatalytic. More generally, this same keto-enol tautomerization can explain how supposed carboxylate radicals avoid decarboxylation in several literature studies. The product aminyl radicals were found to be susceptible to β-fragmentation, releasing alkyl radicals and affording imines. Under radical conditions, these imines are susceptible to allylic H-abstraction and further β-fragmentation leading to dialkyl pyridines as the ultimate degradation products.

ASSOCIATED CONTENT

Supporting Information

Supplementary figures and complete computational details. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of Interest

PN is an employee of BASF, and MLC acknowledges BASF funding for the work.

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REFERENCES

1. Polypropylene. In *Ullmann's Encyclopedia of Industrial Chemistry*, pp 1-44.
2. Tzoganakis, C.; Tang, Y.; Vlachopoulos, J.; Hamielec, A. E., Controlled Degradation of Polypropylene: A Comprehensive Experimental and Theoretical Investigation. *Polym.-Plast. Technol.* **1989,** *28*, 319-350.
3. Coutinho, F. M. B.; Costa, T. H. S., Controlled degradation of polypropylene in solution by organic peroxides. *Polym. Test.* **1994,** *13*, 363-366.
4. Al-Malaika, S., Oxidative degradation and stabilisation of polymers. *Int. Mater. Rev.* **2003,** *48*, 165-185.
5. Tzoganakis, C.; Vlachopoulos, J.; Hamielec, A. E., Production of controlled-rheology polypropylene resins by peroxide promoted degradation during extrusion. *Polym. Eng. Sci.* **1988,** *28*, 170-180.
6. Bremner, T.; Rudin, A.; Cook, D. G., Melt flow index values and molecular weight distributions of commercial thermoplastics. *J. Appl. Poly. Sci.* **1990,** *41*, 1617-1627.
7. Sanchez, J. M., T. N., *Polymeric Materials Encyclopedia*. CRC Press: Boca Raton, 1996; Vol. 7.
8. Bertin, D.; Leblanc, M.; Marque, S. R. A.; Siri, D., Polypropylene degradation: Theoretical and experimental investigations. *Poly. Deg. and Stab.* **2010,** *95*, 782-791.
9. M. Roth, R. P., P. Nesvadba, M.-O. Zink Hydroxylamine esters as polymerization initiators. PCT Int. Appl. **2001** WO 2001090113, November 29, 2001
10. J. Fink, M. R., R. Pfaendner, P. Nesvadba, A. Kramer Method of grafting ethylenically unsaturated carboxylic acid derivatives onto thermoplastic polymers using hydroxylamine esters. PCT Int. Appl. **2002** WO 2002092653A1, November 21, 2002
11. H. Kura, K. S., K. Kunimoto, P. Nesvadba, M. Ohwa Photoresist composition. PCT Int. Appl. **2010** WO2010108835A1, September 30, 2010
12. J.-P. Wolf, L. M., P. Nesvadba, S. Zeren Coating composition comprising hydroxylamine ester initiators and IR/UV curing of coatings. PCT Int. Appl. **2004** WO2004081100A1, September 23, 2004
13. M. Roth, D. S., G. Leslie, P. Nesvadba, R. E. King, N. Kaprinidis Flame retardant polymer compositions containing hydroxylamine esters. PCT Int. Appl. **2003** WO 2003087211A2, October 23, 2003
14. M. Roth, P. N., D. E. Horst Degradation of polypropylene with hydroxylamine ester compositions. PCT Int. Appl. **2006** WO 2006027327, March 16, 2006
15. Nesvadba, P., Radicals and Polymers. *CHIMIA* **2018,** *72*, 456-476.
16. Henry-Riyad, H.; Tidwell, T. T., Thermolysis of N-tetramethylpiperidinyl triphenylacetate: homolytic fragmentation of a TEMPO ester. *J. Phys. Org. Chem.* **2003,** *16*, 559-563.
17. Bélékian, D.; Cassagnau, P.; Flat, J.-J.; Quinebeche, S.; Autissier, L.; Bertin, D.; Siri, D.; Gigmes, D.; Guillaneuf, Y.; Chaumont, P., et al., N-Acetoxy-phthalimide (NAPI) as a new H-abstracting agent at high temperature: application to the melt functionalization of polyethylene. *Polym. Chem.* **2013,** *4*, 2676-2679.
18. Nesvadba, P., N-Alkoxyamines: Synthesis, Properties, and Applications in Polymer Chemistry, Organic Synthesis, and Materials Science. *CHIMIA* **2006,** *60*, 832-840.
19. Nicolas, J.; Guillaneuf, Y.; Lefay, C.; Bertin, D.; Gigmes, D.; Charleux, B., Nitroxide-mediated polymerization. *Prog. Polym. Sci.* **2013,** *38*, 63-235.
20. Gaudel-Siri, A.; Siri, D.; Tordo, P., Homolysis of N-alkoxyamines: A Computational Study. *ChemPhysChem* **2006,** *7*, 430-438.
21. Hodgson, J. L.; Roskop, L. B.; Gordon, M. S.; Lin, C. Y.; Coote, M. L., Side Reactions of Nitroxide-Mediated Polymerization: N–O versus O–C Cleavage of Alkoxyamines. *J. Phys. Chem. A* **2010,** *114*, 10458-10466.
22. Herk, L.; Feld, M.; Szwarc, M., Studies of "Cage" Reactions. *J. Am. Chem. Soc.* **1961,** *83*, 2998-3005.
23. Martin, J. C.; Taylor, J. W.; Drew, E. H., The Decomposition of Acetyl Peroxide in Olefinic Solvents. The Acetyl Peroxide-Cyclohexene Reaction. *J. Am. Chem. Soc.* **1967,** *89*, 129-135.
24. Shine, H. J.; Waters, J. A.; Hoffman, D. M., The Decomposition of Acetyl Peroxide in Solution. III. Kinetics and Use of Radical Traps. *J. Am. Chem. Soc.* **1963,** *85*, 3613-3621.
25. Taylor, J. W.; Martin, J. C., Cage reactions in the thermal decomposition of acetyl peroxide. *J. Am. Chem. Soc.* **1967,** *89*, 6904-6911.
26. Fraind, A.; Turncliff, R.; Fox, T.; Sodano, J.; Ryzhkov, L. R., Exceptionally high decarboxylation rate of a primary aliphatic acyloxy radical determined by radical product yield analysis and quantitative 1H-CIDNP spectroscopy. *J. Phys. Org. Chem.* **2011,** *24*, 809-820.
27. Guillet, J. E.; Gilmer, J. C., Decomposition of lauroyl, decanoyl, and octanoyl peroxides in solution. *Can. J. Chem.* **1969,** *47*, 4405-4411.
28. Skell, P. S.; May, D. D., Ground- and excited-state carboxylate radical chain carriers. Radical chain substitution reactions with acyl hypohalites. *J. Am. Chem. Soc.* **1983,** *105*, 3999-4008.
29. Kharasch, M. S.; Gladstone, M. T., Reactions of Atoms and Free Radicals in Solution. IV. Decomposition of Acetyl Peroxide in Aliphatic Acids—A New Synthesis of Succinic Acid and its Substitution Derivatives. *J. Am. Chem. Soc.* **1943,** *65*, 15-17.
30. Skell, P. S.; May, D. D., .pi.- and .sigma.-Acetoxy radicals. *J. Am. Chem. Soc.* **1981,** *103*, 967-968.
31. Wang, X.-B.; Woo, H.-K.; Wang, L.-S.; Minofar, B.; Jungwirth, P., Determination of the Electron Affinity of the Acetyloxyl Radical (CH3COO) by Low-Temperature Anion Photoelectron Spectroscopy and ab Initio Calculations. *J. Phys. Chem. A* **2006,** *110*, 5047-5050.
32. Rakotonirina, M. D.; Baron, M.; Siri, D.; Gaudel-Siri, A.; Quinebeche, S.; Flat, J.-J.; Gigmes, D.; Cassagnau, P.; Beyou, E.; Guillaneuf, Y., Acyloxyimide derivatives as efficient promoters of polyolefin C–H functionalization: application in the melt grafting of maleic anhydride onto polyethylene. *Polym. Chem.* **2019,** *10*, 4336-4345.
33. Ananchenko, G. S.; Fischer, H., Decomposition of model alkoxyamines in simple and polymerizing systems. I. 2,2,6,6-tetramethylpiperidinyl- N-oxyl-based compounds. *J. Polym. Sci. Part A Polym. Chem.* **2001,** *39*, 3604-3621.
34. Marshall, D. L.; Christian, M. L.; Gryn'ova, G.; Coote, M. L.; Barker, P. J.; Blanksby, S. J., Oxidation of 4-substituted TEMPO derivatives reveals modifications at the 1- and 4-positions. *Org. Biomol. Chem.* **2011,** *9*, 4936-4947.
35. Gryn' ova, G.; Ingold, K. U.; Coote, M. L., New Insights into the Mechanism of Amine/Nitroxide Cycling during the Hindered Amine

Light Stabilizer Inhibited Oxidative Degradation of Polymers. *J. Am. Chem. Soc.* **2012,** *134*, 12979-12988.

36. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H., et al. *Gaussian 09 Rev. D.01*, Wallingford, CT, 2016.

37. Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schü tz, M.; Celani, P.; Györffy, W.; Kats, D.; Korona, T.; Lindh, R., et al. *Molpro, version 2015.1, A Package of Ab Initio Programs*, 2015.

38. Coote, M. L.; Lin, C. Y.; Beckwith, A. L. J.; Zavitsas, A. A., A comparison of methods for measuring relative radical stabilities of carbon-centred radicals. *Phys. Chem. Chem. Phys.* **2010,** *12*, 9597-9610.

39. Hodgson, J. L.; Lin, C. Y.; Coote, M. L.; Marque, S. R. A.; Matyjaszewski, K., Linear Free-Energy Relationships for the Alkyl Radical Affinities of Nitroxides: A Theoretical Study. *Macromolecules* **2010,** *43*, 3728-3743.

40. Zhao, Y.; Truhlar, D. G., The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-class Functionals and 12 Other Functionals. *Theor. Chem. Acc* **2007,** *120*, 215-241.

41. Henry, D. J.; Sullivan, M. B.; Radom, L., G3-RAD and G3X-RAD: Modified Gaussian-3 (G3) and Gaussian-3X (G3X) procedures for radical thermochemistry. *J. Chem. Phys.* **2003,** *118*, 4849-4860.

42. Izgorodina, E. I.; Brittain, D. R. B.; Hodgson, J. L.; Krenske, E. H.; Lin, C. Y.; Namazian, M.; Coote, M. L., Should Contemporary Density Functional Theory Methods Be Used to Study the Thermodynamics of Radical Reactions? *J. Phys. Chem. A* **2007,** *111*, 10754-10768.

43. Coote, M. L.; Krenske, E. H.; Izgorodina, E. I., Computational Studies of RAFT Polymerization – Mechanistic Insights and Practical Applications. *Macromol. Rapid Commun.* **2006,** *27*, 473-497.

44. Ho, J.; Klamt, A.; Coote, L. M., Comment on the Correct Use of Continuum Solvent Models. *J. Phys. Chem. A* **2010,** *114*, 13442-13444.

45. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009,** *113*, 6378-6396.

46. Inokuchi, T.; Kawafuchi, H., Alkylation, Aldol, and Related Reactions of O-Alkanoyl- and 2-AlkenoylTEMPOs (2,2,6,6-Tetramethylpiperidine-N-oxyl): Insight into the Reactivity of Their Anionic Species in Comparison with Esters and Amides. *J. Org. Chem.* **2007,** *72*, 1472-1475.

47. McNaught, A. D.; Wilkinson, A., *IUPAC. Compendium of Chemical Terminology 2nd ed. (the "Gold Book")*. Blackwell Scientific Publications: Oxford, 1997.

48. Luo, Y.-R., *Handbook of Bond Dissociation Energies in Organic Compounds*. CRC Press: Boca Raton, 2002.

49. Koenig, T.; Wielesek, R., Decomposition of acetyl peroxide in the presence of acetate salts. *J. Am. Chem. Soc.* **1969,** *91*, 2551-2557.

50. Bordwell, F. G., Equilibrium acidities in dimethyl sulfoxide solution. *Acc. Chem. Res.* **1988,** *21*, 456–463.

51. Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J., The pKa and keto-enol equilibrium constant of acetone in aqueous solution. *J. Am. Chem. Soc.* **1984,** *106*, 460–462.

52. Serjeant, E. P.; B., D., *Ionisation Constants of Organic Acids in Aqueous Solution.* . Pergamon Press: New York, 1979; Vol. 23.

53. K ü tt, A.; Selberg, S.; Kaljurand, I.; Tshepelevitsh, S.; Heering, A.; Darnell, A.; Kaupmees, K.; Piirsalu, M.; Leito, I., pKa values in organic chemistry – Making maximum use of the available data. *Tetrahedron Lett.* **2018,** *59*, 3738-3748.

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