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Regeneration of Amine in Catalytic Inhibition of Oxidation[†]

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Kinetic and mechanistic investigations of hexadecane autoxidation inhibited by 4,4′-dioctyldiphenylamine, Ar_2NH, and (4,4′-dioctyldiphenylamino)-*N*-oxy, $Ar_2NO^{\bullet}$, at 160 °C showed that $Ar_2NO^{\bullet}$ is a reactive intermediate formed during oxidation inhibited by Ar_2NH and that Ar_2NH is formed during oxidation inhibited by $Ar_2NO^{\bullet}$. Investigations of decomposition of *N*-(*sec*-hexadecyloxy)- and *N*-(3-heptyloxy)-4,4′-dioctyldiphenylamines, Ar_2NOR, formed from $Ar_2NO^{\bullet}$, showed that at temperatures above 120 °C these compounds rapidly decompose to yield Ar_2NH. These results suggest that during the inhibition of oxidation by aromatic secondary amines or the corresponding nitroxide radicals at elevated temperatures the decomposition of *N*-*sec*-alkoxydiarylamines leads to regeneration of the parent aromatic secondary amine. Thus, amine regeneration is a principal step in the catalytic inhibition of oxidation by aromatic secondary amines or the corresponding nitroxide radicals. This catalytic inhibition process explains the high stoichiometric inhibition factors observed with these compounds.

Introduction

A variety of mechanisms have been proposed to account for the ability of secondary amines to inhibit the autoxidation of hydrocarbons at elevated temperatures. Most mechanisms can fit within the general framework of the following reaction scheme.[1−4] In reaction 1, amine (>NH)

$$>NH \longrightarrow >NO^{\bullet} + \text{products} \qquad (1)$$

$$\left.\begin{array}{l} >NO^{\bullet} + R^{\bullet} \longrightarrow >NOR \\ >NOR \longrightarrow >NO^{\bullet} + \text{product} \end{array}\right\} \begin{array}{c}\text{regeneration}\\ \text{cycle}\end{array} \qquad \begin{array}{c}(2)\\(3)\end{array}$$

is oxidized to nitroxide ($>NO^{\bullet}$). In reaction 2, nitroxide reacts to scavenge carbon-centered radicals and yield alkoxyamine ($>NOR$) products. The high stoichiometric efficiency, $f > 40$, usually observed for secondary amine antioxidants, has been attributed to the regeneration of nitroxide from alkoxy amines, reaction 3.[1,3] The present work will suggest that at elevated temperatures the high stoichiometric efficiency observed with secondary amine antioxidants, $f > 12$, must be to a significant degree due to the regeneration of parent amine from alkoxy amines.

Experimental Section

Reagents. 4,4′-Dioctyldiphenylamine (IRGANOX L01), Ar_2NH, was obtained from Ciba-Geigy and used without further purification. (4,4′-Dioctyldiphenylamino)-*N*-oxy, $Ar_2NO^{\bullet}$, was synthesized according to the procedure outlined below. Hexadecane (99%), *p*-nitroperbenzoic acid, and (4-hydroxy-2,2,6,6-tetramethylpiperidinyl)-*N*-oxy (TEMPOL) were obtained from Aldrich Chemical Co. Hexadecane was purified by percolation through silica gel and alumina under argon and then stored under argon.[5] TEMPOL was recrystallized three times from hexane prior to use. *tert*-Butyl peroxy-2-ethylhexanoate, TBPO, was obtained from Akzo. High-performance liquid chromatography, HPLC, experiments were carried out with Burdick and Jackson distilled-in-glass grade solvents.

Synthesis of $Ar_2NO^{\bullet}$. Excess *p*-nitroperbenzoic acid was added in dropwise fashion to 1.02 g (0.0026 mol) of Ar_2NH in benzene solution at room temperature. The red reaction mixture was stirred for 2 h after the addition was complete. The reaction mixture was transferred to a separatory funnel and washed with aqueous Na_2CO_3 to remove benzoic acid and excess peracid. Benzene was then removed by rotary evaporation. The oily residue that remained was passed through an alumina column with 20% (v/v) CH_2Cl_2 in hexane. The elution solvents were removed by rotary evaporation, and the red solid residue was recrystallized from CH_3OH (mp 68.5 °C) to yield 0.45 g (0.0011 mol) of $Ar_2NO^{\bullet}$.

HPLC analysis of the crystalline solid revealed a single peak at an elution volume, V_E, of 17.8 mL (see below for HPLC conditions). The electron spin resonance, ESR, spectrum of the crystalline solid in freeze-thaw-degassed benzene solution is consistent with a bis(*p*-*tert*-alkyldiaryl) nitroxide, namely, $a_N = 10.2$ G, $a_{4H(o)} = 1.9$ G, and $a_{4H(m)} = 0.8$ G.[6,7]

Product Analysis. HPLC was used to determine the concentration of Ar_2NH and $Ar_2NO^{\bullet}$ and the relative concentration of Ar_2NOR (corresponding alkoxy amines) in hexadecane reaction mixtures. HPLC analysis was performed using solvent programming with a low-pressure mixer (Micromeritics Models 750 and 752), a Waters U6K injector and Z-Module cartridge system (C-18 cartridge), and variable wavelength UV/vis detector (Beckman Model 165) operating at 280 and 320 nm. The detection wavelengths were chosen to maximize the detection of Ar_2NH and $Ar_2NO^{\bullet}$ and minimize interference from the nonaromatic hexadecane oxidation products. Solvent composition was programmed from 10:10:80 (CH_3OH:H_2O:CH_3CN) to 20:80 (CH_2Cl_2:CH_3CN). Elution volumes, V_E, for analyzed compounds are listed in Table 1. $Ar_2NO^{\bullet}$ was identified by direct comparison with a sample of $Ar_2NO^{\bullet}$ synthesized independently as described above. The peak due to $Ar_2NO^{\bullet}$ is not well separated from that due to Ar_2NH, but the absorbance ratios of the two compounds, A_{280}/A_{320}, are sufficiently different, i.e., 0.34 and 3.5, respectively, to allow the concentration of Ar_2NH to be accurately determined and $Ar_2NO^{\bullet}$ to be estimated. ESR proved to be the more accurate means to quantify $Ar_2NO^{\bullet}$, and therefore, the ESR

[†] Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday.

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Table 1. HPLC Elution Volumes and Peak Assignments

V_E (mL)	A_{280}/A_{320}	assignment
17.8	0.34	$Ar_2NO^•$
18.6	3.5	Ar_2NH
25	1.8	unknown I
28	5.5	Ar_2NOR ($R = C_7$)
40	2.6	unknown II
~53	4	Ar_2NOR ($R = C_{16}$)
~55	~1.3	unknown III

method was preferentially used to determine the concentration of $Ar_2NO^•$ in this work (see below).

Gas−liquid chromatography, GLC, was used to determine the concentration of isomeric hexadecanone oxidation products. The GLC procedure has been previously described.[8]

Gas chromatography−mass spectrometry, GC−MS, analysis was used to verify that the HPLC peak at V_E = 18.6 mL observed during the nitroxide-inhibited oxidation of hexadecane at 160 °C in the presence of oxygen was Ar_2NH. GC−MS analysis was performed using a Hewlett-Packard Model 5987 GC−MS. A 1 μL splitless injection was used. The oven temperature was programmed from 40 to 300 °C with a heating rate of 4 °C/min and held at 300 °C for 30 min. The mass spectrum was scanned from 50 to 750 amu.

GC−MS was used to identify Ar_2NH in a sample taken from the oxygen-free 120 °C decomposition of TBPO in hexadecane containing $Ar_2NO^•$. The sample was first passed through silica and C-18 SEP-PAK cartridges (Waters Associates) to remove hexadecane and hexadecane oxidation products. The mass spectrum of the major GLC peak in this eluent was found to be identical to that of authentic Ar_2NH. Ar_2NH exhibits a parent ion peak at m/e = 393 and a large parent minus 71 peak corresponding to fragmentation at the carbon α to the aromatic ring and loss of a C_5H_{11} group.

ESR spectrometry was used to determine the concentration of $Ar_2NO^•$ in hexadecane inhibited with either Ar_2NH or $Ar_2NO^•$. ESR spectra were recorded with a Bruker ER 200D ESR spectrometer equipped with an Aspect 2000 data system. The concentration of $Ar_2NO^•$ in unknown samples was determined by direct comparison with known amounts of TEMPOL in hexadecane solution. Comparison was made on the basis of double integral areas of the first derivative ESR signals. The same 6-mm o.d. quartz tube was used for all samples. ESR spectra were recorded at constant modulation amplitude and power settings of 4 G and 6.5 mW, respectively.

Hydroperoxide concentration was determined by iodometric titration using a Metrohm titroprocessor according to procedures previously described.[5]

Hexadecane Oxidation. Hexadecane oxidations were carried out using a batch reactor system previously described.[9]

Results

In Figure 1 the concentration of hydroperoxide to the half power, $[-OOH]^{1/2}$, which is proportional to the oxidation rate,[10] is plotted versus time for the 160 °C oxidation of hexadecane in the presence and absence of inhibitor Ar_2NH. In the absence of Ar_2NH, the oxidation rate increases linearly with time (dashed line, upper plot). When Ar_2NH (0.38 mM) is added to hexadecane that has been preoxidized to contain ~11 mM of hydroperoxide, the increase of oxidation rate is suppressed by a factor of ~3, but not reduced to zero. During this inhibited oxidation, hydroperoxide concentration and therefore the rate of free radical initiation[11] continues to increase. At the end of the inhibited oxidation, the increase of oxidation rate approaches that prior to the addition of Ar_2NH since the slope of the curve after ~5000 s is appoximately equal to that of the uninhibited oxidation.

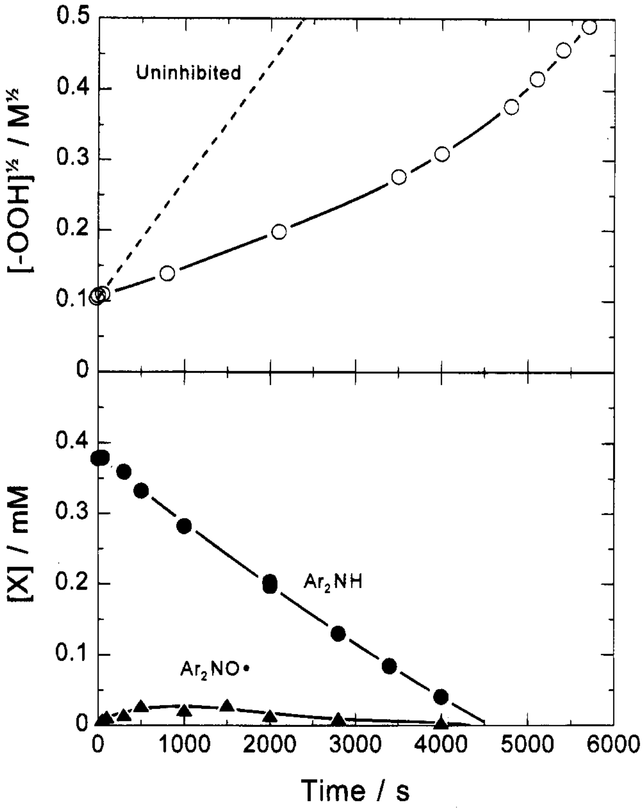

Figure 1. Inhibition of oxidation with Ar_2NH: $[-OOH]_0$ = 11 mM, $[Ar_2NH]_0$ = 0.38 mM.

HPLC analysis of the reaction mixture withdrawn during the inhibited oxidation reveals the presence of unreacted Ar_2NH, $Ar_2NO^•$, and a number of polar components with low elution volumes. Nonpolar alkoxyamine (Ar_2NOR) components are not detected. The changes of concentration of Ar_2NH and $Ar_2NO^•$ during inhibited oxidation are shown in the bottom part of Figure 1. Comparison between upper and lower plots reveals that the autocatalytic uninhibited oxidation resumes when Ar_2NH and $Ar_2NO^•$ have been completely consumed. During the inhibited oxidation the concentration of $Ar_2NO^•$ never exceeds 0.03 mM, or 9% of the total Ar_2NH initially added.

When the above experiment is repeated with substitution of an equal molar amount of $Ar_2NO^•$ for the Ar_2NH, the oxidation rate is suppressed to approximately the same degree as with the Ar_2NH, Figure 2. Surprisingly, a large fraction, >54%, of the total $Ar_2NO^•$ added is converted to Ar_2NH well before the uninhibited oxidation resumes, lower plot, Figure 2. The concentration of $Ar_2NO^•$ drops below 0.004 mM well before the end of the inhibited oxidation. Again, there is no evidence for the presence of any Ar_2NOR components.

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(10) The rate of formation of hydroperoxides can be expressed by $d[-OOH]/dt = k_c[RH][-OOH]^{1/2}$ where k_c is a composite rate constant (see ref 5 for detailed kinetics). This expression can be integrated to give $[-OOH]_t^{1/2} = (k_c/2)[RH]t$.

(11) The rate of the reaction of the inhibitor with the radicals present in the system is not fast enough to completely suppress the propagation reactions resulting in an increase of hydroperoxides.

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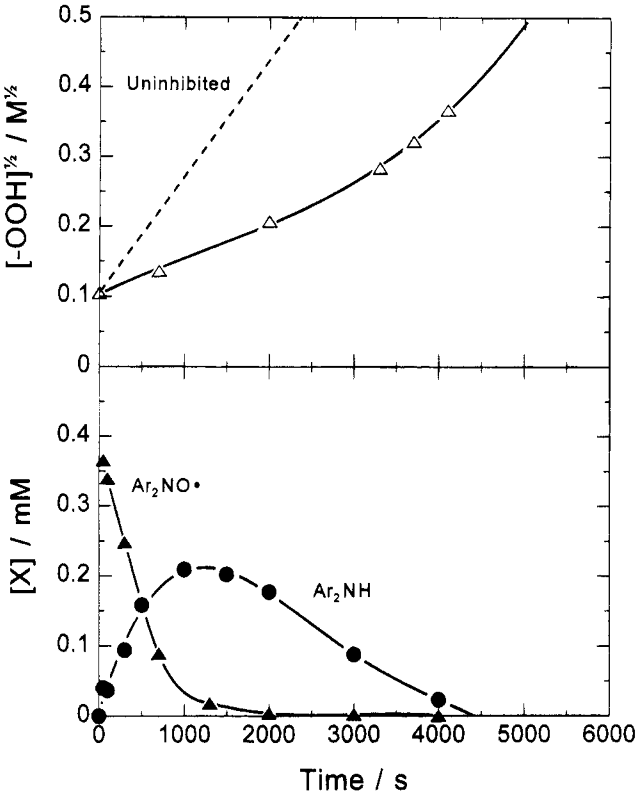


Figure 2. Inhibition of oxidation with $Ar_2NO^{\bullet}$: $[-OOH]_0$ = 11 mM, $[Ar_2NO^{\bullet}]_0$ = 0.41 mM.

The influence of oxygen concentration in the oxidizing gas on the conversion of $Ar_2NO^{\bullet}$ to Ar_2NH is shown in Figure 3. When the oxygen concentration is reduced from 100% to 10%, the peak conversion of $Ar_2NO^{\bullet}$ to Ar_2NH goes from ~45% to ~70% and the rate of disappearance of $Ar_2NO^{\bullet}$ is increased by about 30%. Again, Ar_2NOR components are not detected.

A series of experiments was carried out to investigate the apparent absence of Ar_2NOR components in inhibited hexadecane oxidations at 160 °C by generating Ar_2NOR in situ at a lower temperature and then following its decay.

When TBPO (~3 mM) is decomposed to 3-heptyl and *tert*-butoxyl radicals in oxygen free hexadecane containing $Ar_2NO^{\bullet}$ at 95 °C under argon, six HPLC peaks are detected; a peak due to unreacted $Ar_2NO^{\bullet}$, a minor peak due to Ar_2NH, two major peaks, and two minor peaks. The concentration of $Ar_2NO^{\bullet}$ and Ar_2NH and relative HPLC responses of the other four components are shown in Figure 4. The two major peaks are assigned to the Ar_2NOR compounds expected from the well known reaction between nitroxides and alkyl radicals,[13,14] namely, *N*-(3-heptyloxy)-4,4′-dioctyldiphenylamine, Ar_2NOR (R = C_7), and isomeric *N*-(*sec*-hexadecyloxy)-4,4′-dioctyldiphenylamines, Ar_2NOR (R = C_{16}). The peak assigned to Ar_2NOR (R = C_7) is sharp, V_E = 28, while that due to Ar_2NOR (R = C_{16}) is a broad envelope, $V_E \approx 53$ mL, implying the expected distribution of seven isomers. The concentration of these Ar_2NOR products increases steadily as $Ar_2NO^{\bullet}$ is consumed. The amount of Ar_2NH formed at 95 °C is much less than that formed in inhibited oxidation at 160 °C.

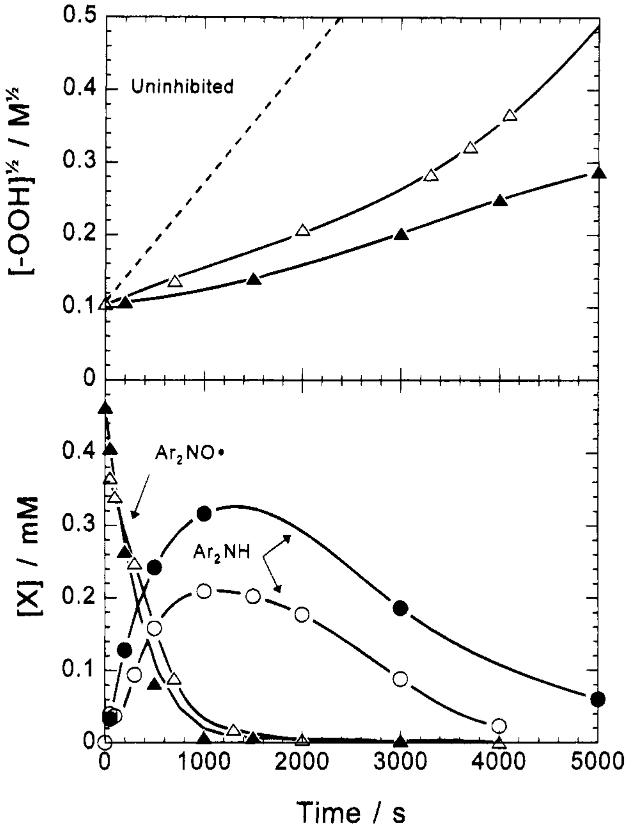


Figure 3. Formation of Ar_2NH under reduced oxygen pressure. Open symbols are at 100% O_2 and filled symbols are at 10% O_2.

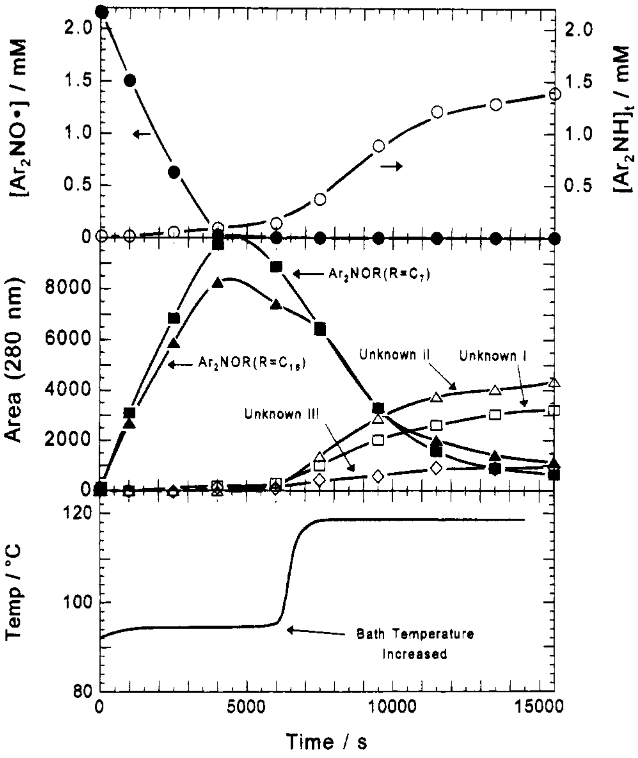
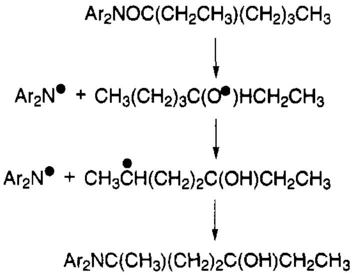


Figure 4. Formation and decomposition of Ar_2NOR under inert atmosphere.

When the concentration of $Ar_2NO^{\bullet}$ decreased to <0.003 mM, the reaction temperature was quickly raised to 120 °C. At 120 °C, the concentration of Ar_2NH increases dramatically until it accounts for 64% of the $Ar_2NO^{\bullet}$ initially added. The concentrations of the two Ar_2NOR products decrease, while the concentrations of unknowns I and II, which are minor at 90 °C, increase along with a third component, unknown III, which is undetected at

90 °C. Like the Ar_2NOR products, unknowns I and II also exhibit greatly different elution volumes; V_E of 25 and 40 mL. Also like the Ar_2NOR products, the HPLC peak due to unknown I is sharp while that due to unknown II is a broad envelope. The exact nature of these two products has not been determined conclusively, but GC–MS analysis of concentrates containing these components indicate parent ions at the same *m/e* as would be expected for the Ar_2NOR compounds. Thus, they may be some form of rearrangement products of the Ar_2NOR species. A reasonable but unverified proposal for the heptyl product suggested by one of the reviewers is given by reaction 4. The third unknown peak is a broad envelope that overlaps with the peaks due to Ar_2NOR ($R = C_{16}$). GC analysis of the reaction mixture after the decomposition of Ar_2NOR species at 120°C revealed the presence of isomeric hexadecanones in an amount ≈1/2 of the concentration of Ar_2NH. 3-Heptanone has also been detected but could not be quantitatively determined due to its volatility (bp 147 °C) under these reaction conditions.


(4)

$$\begin{array}{c} Ar_2NOC(CH_2CH_3)(CH_2)_3CH_3 \\ \downarrow \\ Ar_2N^\bullet + CH_3(CH_2)_3C(O^\bullet)HCH_2CH_3 \\ \downarrow \\ Ar_2N^\bullet + CH_3\overset{\bullet}{C}H(CH_2)_2C(OH)CH_2CH_3 \\ \downarrow \\ Ar_2NC(CH_3)(CH_2)_2C(OH)CH_2CH_3 \end{array} \qquad (4)$$

Discussion

It is well recognized that the antioxidant activity of many secondary amines arises through a complex series of dynamic equilibria that involve free radical intermediates derived from the antioxidant, the hydrocarbon oxidized, and their corresponding termination products.[1,3,14] As a result, it is difficult to relate the concentration behavior of individual species in the resultant reaction mixture to specific reactions. At best, the concentration behavior of individual species reveals their relative reactivity, in which order the species are being formed, and whether they are intermediates or final reaction products. An increase in concentration of any given intermediate indicates that the rate of formation of the species is greater than its rate of decay and vice versa.

In the present work, the concentration behavior of the parent amine antioxidant, its nitroxide, alkoxy amine adducts, and hexadecane oxidation products were followed. The concentration behavior of these products suggests that regeneration of parent amine from alkoxy amine intermediates, reaction 5, plays a key role in the

$$>NOR \xrightarrow{\Delta} >NH + \text{products} \qquad (5)$$

inhibition chemistry of secondary amine antioxidants during inhibited oxidation of hexadecane at elevated temperatures. This reaction has not been previously recognized; however, the conversion of $>NCH_3$ to $>NH$ in the photooxidation of polypropylene[15] and $>NO^\bullet$ to $>NH$ in the photooxidation of acrylic/melamine coatings[16] have been previously reported. The mechanisms of those conversions are not known but could involve the comparable $>NOPP$ and $>NOC(OH)$ intermediates.

The plots shown in Figure 1 compare antioxidant consumption with product behavior when Ar_2NH is added to oxidizing hexadecane at 160 °C. Under these conditions, Ar_2NH partially inhibits the oxidation. This inhibition ceases when Ar_2NH is completely consumed. Comparison between the rate of free radical trapping[17] ($R_t = 5.1 \times 10^{-7}$ M s^{-1} at the point of addition, rising to $R_t = 2.6 \times 10^{-6}$ M s^{-1} at 4000 s) and the rate of decay of Ar_2NH ($-d[Ar_2NH]/dt = 9.1 \times 10^{-8}$ M s^{-1} at the point of addition and 7.2×10^{-8} M s^{-1} at 4000 s) suggests that the Ar_2NH decay rate should be 5.6 to 36 times faster if the stoichiometric factor for Ar_2NH would be equal to 1. Of course, on the basis of this assumption, it is not possible to conclude that Ar_2NH is being regenerated, because inhibition by $Ar_2NO^\bullet$ and other possible undetected inhibitors, alkoxyamines for example, could account for the reduced rate of Ar_2NH decay. $Ar_2NO^\bullet$ can be detected over the course of the inhibited oxidation at a low concentration which first increases and then decreases. However, only a small fraction of the total Ar_2NH initially added can be accounted for as nitroxide. The sustained low concentration of $Ar_2NO^\bullet$ observed provides clear evidence that nitroxide is being regenerated from its reaction products as has been previously concluded.[1,3] The rate of initiation of free radicals due to hydroperoxide thermolysis would be sufficient to consume all of the nitroxide present in a very brief period if this were not the case.

When $Ar_2NO^\bullet$ is substituted for Ar_2NH in the oxidation experiment above, large quantities of Ar_2NH are observed as a reaction product. This firmly establishes that a reaction path exists to convert $Ar_2NO^\bullet$ or its reaction products to Ar_2NH, Figure 2. The conversion is rapid, and Ar_2NH builds to a surprisingly high concentration. The high concentration of Ar_2NH observed suggests that it may be the least reactive inhibitor present in the system and that its rate of regeneration is high. The initial rate of decay of $Ar_2NO^\bullet$ is about five times that observed for Ar_2NH in the previous experiment (5×10^{-7} M s^{-1} vs 9.1×10^{-8} M s^{-1}) and it approximately corresponds to the rate of radical formation (6.2×10^{-7} M s^{-1}). Despite the above difference in the rates of decay, the rate of oxidation of hexadecane is inhibited to the same degree in both cases, but the induction period with $Ar_2NO^\bullet$ is slightly shorter than with Ar_2NH. An explanation of these observations may lie in the facts that nitroxides are known to readily scavenge carbon-centered radicals while amines are thought to be most reactive toward peroxyl radicals[1] and that the formation of $Ar_2NO^\bullet$ from Ar_2NH is a slower process while the regeneration of Ar_2NH from $Ar_2NO^\bullet$ or its products is fast. It is clear that a different concentration balance exists in the inhibitor mix in the initial stages of inhibited oxidation when $Ar_2NO^\bullet$ is substituted for Ar_2NH. Nevertheless, the overall outcome of inhibition is the same in both cases.

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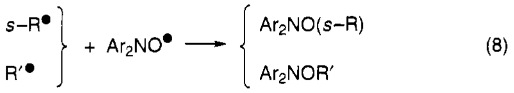
[17] The rate of free radical trapping, R_t, is a fraction of the rate of free radical formation, R_i, corresponding to a decrease in oxidation rate due to inhibition. Thus, $R_t = R_i(\alpha_{uninh} - \alpha_{inh})/\alpha_{uninh}$, where α_{uninh} and α_{inh} are slopes of the oxidation curves in Figure 1.

As is illustrated in Figure 3, the composition of the inhibitor mix is very sensitive to oxygen concentration. The $Ar_2NO^\bullet$ decay at reduced oxygen concentration is faster by a factor of ~2 (9.7×10^{-7} M s^{-1} vs 5×10^{-7} M s^{-1}). This is probably due to the lower steady state concentration of $RO_2^\bullet$ radicals relative to $R^\bullet$ radicals at lower oxygen pressure. The lower steady state concentration of $RO_2^\bullet$ is also reflected in the enhanced rate of inhibition of oxidation under these conditions.

A final series of experiments was carried out to determine the manner in which $Ar_2NO^\bullet$ is converted to Ar_2NH. TBPO was decomposed at 95 °C in oxygen free hexadecane containing $Ar_2NO^\bullet$, Figure 4. Under these conditions, the decomposition of the perester leads to the formation of 3-heptyl and *tert*-butoxyl radicals, reaction 6, followed by hydrogen atom abstraction from hexadecane by *tert*-butoxyl radical resulting in the formation of isomeric *sec*-hexadecyl radicals, *s*-R•, reaction 7. In the absence of oxygen, the carbon-centered radicals can be scavenged by $Ar_2NO^\bullet$ to yield the corresponding alkoxy amines, reaction 8. As can be seen in Figure 4, middle panel, alkoxyamines rapidly build to a high concentration during the early stages of perester decomposition while $Ar_2NO^\bullet$ is available. The concentration of alkoxyamines begin to decrease when $Ar_2NO^\bullet$ is depleted. The decrease may be due to continued reaction with perester decomposition products or thermolysis as will be suggested shortly. A small amount of Ar_2NH is detectable from the onset of the reaction as are two unidentified products. When $Ar_2NO^\bullet$ was completely consumed, the reaction temperature was abruptly raised from 95 to 120 °C. At this point ~80% of the perester initially added should have decomposed (estimated from half-life data: $t_{1/2}$ = 45 min at 95 °C).[18] At 120 °C the residual perester should be quickly decomposed ($t_{1/2}$ = 3 min). The temperature increase dramatically accelerates the formation of Ar_2NH, the formation of unknowns I–III, and the decay of alkoxyamines. As can be seen, the decay of alkoxyamines and formation of Ar_2NH and unknowns I–III continues long after the perester has been depleted suggesting that the decomposition of alkoxyamines is not radical induced under these conditions.

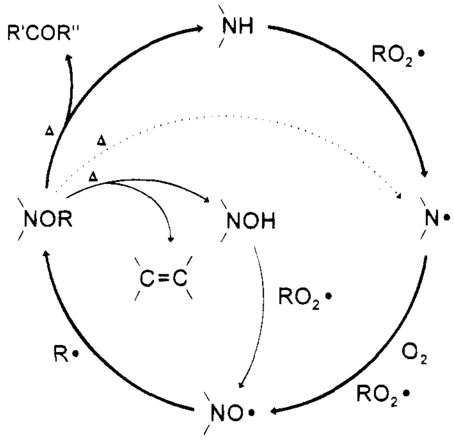
$$\underset{\text{(TBPO)}}{CH_3CH_2C(CH_3(CH_2)_2CH_2)HC(O)O_2C(CH_3)_3} \xrightarrow{\Delta} \underset{(R'^\bullet)}{CH_3CH_2{}^\bullet C(CH_3(CH_2)_2CH_2)H} + CO_2 + \underset{(t\text{-}BuO^\bullet)}{{}^\bullet OC(CH_3)_3} \tag{6}$$

$$t\text{-}BuO^\bullet + s\text{-}RH \rightarrow t\text{-}BuOH + s\text{-}R^\bullet \tag{7}$$



$$\left.\begin{matrix} s\text{-}R^\bullet \\ R'^\bullet \end{matrix}\right\} + Ar_2NO^\bullet \longrightarrow \left\{\begin{matrix} Ar_2NO(s\text{-}R) \\ Ar_2NOR' \end{matrix}\right. \tag{8}$$

Scheme 1. Mechanism for the Catalytic Inhibition by Ar_2NH and $Ar_2NO^\bullet$



Catalytic Inhibition Mechanism. A proposed mechanism for the catalytic inhibition by Ar_2NH and $Ar_2NO^\bullet$ which explains the products detected for autoxidations involving secondary radicals is shown in Scheme 1. In this mechanism the amine is first oxidized to the nitroxide radical. This can be accomplished by abstraction of hydrogen from Ar_2NH by a peroxyl radical forming a hydroperoxide and the aminyl radical, $Ar_2N^\bullet$. $Ar_2N^\bullet$ can then react with another peroxyl radical to yield $Ar_2NO^\bullet$ and an alkoxyl radical.[19] The secondary alkyl radical can react with $Ar_2NO^\bullet$ to form the *N*-*sec*-alkoxydiarylamine which decomposes thermally, leading to formation of ketones and Ar_2NH completing the inhibition cycle. One complete inhibition cycle traps two radicals (one peroxyl and one alkyl). The side reactions such as peroxyl radical addition to $Ar_2NO^\bullet$ leading to nonradical products would stop the catalytic inhibition chain.

This mechanism differs from that proposed for tertiary radicals in the pathway of decomposition of the *N*-alkoxydiarylamine. Denisov[3] has previously suggested that a variety of cyclic inhibition mechanisms exist depending on the structure of the amine. Our results clearly show that the mechanism is also strongly affected by the structure of the hydrocarbon substrate derived radicals produced during the oxidation.

Our results show that in oxidation systems where secondary alkyl radicals are formed, the catalytic cycle of inhibition by aromatic secondary amines and the corresponding nitroxide radicals at elevated temperatures involves regeneration of the parent amine. This regeneration occurs due to the thermal decomposition of intermediate *N*-*sec*-alkoxydiarylamines. The products of this thermal decomposition are ketones and the parent amine.

Acknowledgment. We wish to thank Dr. K. U. Ingold for his helpful comments during the preparation of this manuscript.

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