Absolute Rate Constants for the Reactions of Primary Alkyl Radicals with Aromatic Amines[1]

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Hydrogen abstraction from diarylamines (4-X-C_6H_4)$_2$NH [X = H, CH_3, C_8H_{17}, CH_3O, and Br] by the 2-methyl-2-phenylpropyl radical in *n*-dodecane solution was investigated by thermolysis of 3-methyl-3-phenylbutanoyl peroxide in the presence of various concentrations of the amines. The reaction is a non-chain process in which the 2-methyl-2-phenylpropyl radical and its rearrangement product, the 2-benzylpropan-2-yl radical, abstract hydrogen from both the solvent and the amine. Cross-disproportionation reactions of the rearranged radical led to the formation of significant amounts of β,β-dimethylstyrene. Rate constants for hydrogen abstraction by the unrearranged, primary alkyl radical from *n*-dodecane ($k^{373K} = 3.5 \times 10^3$ M^{-1} s^{-1}), diphenylamine ($k^{373K} = 1.3 \times 10^6$ M^{-1} s^{-1}), and the substituted diarylamines were determined from the product yields and the known rate constant for the radical rearrangement. From kinetic experiments with *N*-deuteriodiphenylamine the deuterium kinetic isotope effect, k_{NH}/k_{ND}, was found to be 2.3 at 373 K.

Diarylamines find extensive use as radical-trapping antioxidants in lubricating oils exposed to high-temperature service conditions such as the oils used in passenger cars and jet engines. The increasing severity under which the new generation of engines are planned to operate will impose increased thermal and oxidative stress on the lubricating fluids. In principle, kinetic modeling studies can provide valuable insights into the overall behavior of oils at high temperatures. This is because reliable modeling can pinpoint critical elementary reactions where a possible chemical modification of the oil or of an additive would produce a change in the critical rate constant with a consequent improvement in the overall stability of the oil/additive system. However, reliable modeling requires accurate rate constants for all the elementary reactions known (or thought to be) involved in these extremely complex systems which are shown in Scheme 1 in grossly simplified form for the diarylamine-inhibited autoxidation of a hydrocarbon, RH.[3] Diarylamines are known to be excellent traps for peroxyl radicals,[5,6] reaction 4 (Scheme 1). However, carbon-centered radicals are also involved in autoxidation which raises the question we address herein: How fast is the reaction of diarylamines with carbon-centered radicals?

Scheme 1

initiation $$\text{In}^\bullet + \text{RH} \rightarrow \text{R}^\bullet \quad (1)$$

propagation $$\text{R}^\bullet + \text{O}_2 \rightarrow \text{ROO}^\bullet \quad (2)$$

$$\text{ROO}^\bullet + \text{RH} \rightarrow \text{ROOH} + \text{R}^\bullet \quad (3)$$

termination

$$\text{ROO}^\bullet + \text{Ar}_2\text{NH} \rightarrow \text{ROOH} + \text{Ar}_2\text{N}^\bullet \quad (4)$$

$$\text{ROO}^\bullet + \text{Ar}_2\text{N}^\bullet \rightarrow \text{nonradical products} \quad (5)$$

$$\text{R}^\bullet + \text{Ar}_2\text{NH} \rightarrow \text{RH} + \text{Ar}_2\text{N}^\bullet \quad (6)$$

Results

The radical-clock method[7] appeared to be the simplest procedure for determining k_6. Preliminary experiments using the 5-hexenyl radical clock showed only that this clock ran "too fast". Thus, even with 2.4 M diphenylamine at 80 °C, by far the major hydrocarbon product was methylcyclopentane with the yield of 1-hexene being too small even for its positive identification. That is, the rearrangement of the 5-hexenyl radical to the cyclopentylmethyl radical is too fast to compete with hydrogen abstraction from the amine. We therefore turned to the much slower neophyl radical clock which was found to be very suitable for our purposes. Thermolysis of 3-methyl-3-phenylbutanoyl peroxide (1.6 × 10^{-3} M) in dodecane at 100 °C yielded *tert*-butylbenzene, isobutylbenzene, and β,β-dimethylstyrene, and more importantly, the yield of *tert*-butylbenzene relative to the other two products increased dramatically upon the addition of diphenylamine at concentrations in the range 0.029−0.10 M. The chemistry which we believe is occurring is portrayed in Scheme 2 with the products of interest indicated in bold face.

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[3] This scheme ignores the complexities introduced by the regeneration of Ar_2NH from its nitroxide, $Ar_2NO^\bullet$, at temperatures ≥130 °C.[4] These complexities can be ignored for our present purposes because our work has been carried out under oxygen-free conditions.

[4] Jensen, R. K.; Korcek, S.; Zinbo, M.; Gerlock, J. L. *J. Org. Chem.* **1995**, *60*, 5396−5400.

[5] (a) Brownlie, I. T.; Ingold, K. U. *Can. J. Chem.* **1966**, *44*, 861−868. (b) Brownlie, I. T.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 2417−2425.

[6] Karpukhin, O. N.; Shlyapintokh, V. Ya.; Zolotova, N. V. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1963**, 1722−1727.

[7] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317−323. For a more recent review, see: Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176.

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Scheme 2

$$[\mathrm{PhCMe_2CH_2C(O)O}]_2 \rightarrow 2\mathrm{PhCMe_2CH_2}^{\bullet} + 2\ \mathrm{CO_2} \qquad (7)$$

$$\mathrm{PhCMe_2CH_2}^{\bullet} + \mathrm{C_{12}H_{26}} \xrightarrow{k_{\mathrm{CH}}} \mathbf{PhCMe_3} + \mathrm{C_{12}H_{25}}^{\bullet} \qquad (8)$$

$$\mathrm{PhCMe_2CH_2}^{\bullet} + \mathrm{Ar_2NH} \xrightarrow{k_{\mathrm{NH}}} \mathbf{PhCMe_3} + \mathrm{Ar_2N}^{\bullet} \qquad (9)$$

$$\mathrm{PhCMe_2CH_2}^{\bullet} \xrightarrow{k_{\mathrm{r}}} \mathrm{PhCH_2\overset{\bullet}{C}Me_2} \qquad (10)$$

$$\mathrm{PhCH_2\overset{\bullet}{C}Me_2} + \mathrm{C_{12}H_{26}} \rightarrow \mathbf{PhCH_2CHMe_2} + \mathrm{C_{12}H_{25}}. \qquad (11)$$

$$\mathrm{PhCH_2\overset{\bullet}{C}Me_2} + \mathrm{Ar_2NH} \rightarrow \mathbf{PhCH_2CHMe} + \mathrm{Ar_2N}^{\bullet} \qquad (12)$$

$$\mathrm{PhCH_2\overset{\bullet}{C}Me_2} + \mathrm{X}^{\bullet} \rightarrow \mathbf{PhCH{=}CMe_2} + \mathrm{XH} \qquad (13)$$

$$(\mathrm{X}^{\bullet} = \mathrm{C_{12}H_{25}}^{\bullet},\ \mathrm{PhCMe_2CH_2}^{\bullet},\ \mathrm{PhCH_2\overset{\bullet}{C}Me_2},\ \mathrm{Ar_2N}^{\bullet})$$

$$\mathrm{C_{12}H_{25}}^{\bullet} + \mathrm{Ar_2NH} \rightarrow \mathrm{C_{12}H_{26}} + \mathrm{Ar_2N}^{\bullet} \qquad (14)$$

$$\mathrm{Ar_2N}^{\bullet} + \mathrm{Ar_2N}^{\bullet} \rightarrow \mathbf{Ar_2NNAr_2} \qquad (15)$$

Two points should be noted about Scheme 2. First, the reaction is not a chain reaction. That is, any radical-induced decomposition of the peroxide could be ignored because esters were not detected among the products.[8] Second, Scheme 2 includes only two radical−radical reactions yielding nonradical products: reaction 13 is required to explain the formation of β,β-dimethylstyrene; reaction 15 is required to account for the fact that tetraarylhydrazines were formed in low yields whereas N-alkylated diphenylamines (i.e., the products of cross-combination) could not be detected.

A simple kinetic analysis of Scheme 2 yields:

$$\frac{[\text{unrearranged product}]}{[\text{rearranged products}]} = \frac{[\mathrm{PhCMe_3}]}{[\mathrm{PhCH_2CHMe_2}] + [\mathrm{PhCH{=}CMe_2}]} = \frac{k_{\mathrm{CH}}[\mathrm{C_{12}H_{26}}] + k_{\mathrm{NH}}[\mathrm{Ar_2NH}]}{k_{\mathrm{r}}} \qquad (\mathrm{I})$$

Thus, a plot of the ratio of the yield of unrearranged product to rearranged products against the amine concentration should give a straight line with a slope equal to $k_{\mathrm{NH}}/k_{\mathrm{r}}$ and an intercept equal to $k_{\mathrm{CH}}[\mathrm{C_{12}H_{26}}]/k_{\mathrm{r}}$. Five experiments were carried out in the absence of diphenylamine and the mean value for the ratio: [unrearranged product]/[rearranged products], viz., 0.33, was combined with the results of experiments carried out at four different concentrations of diphenylamine (see Table 1) to construct the plot (circles) shown in Figure 1.[10]

Similar experiments were carried out with N-deuterated diphenylamine,[5,11] and the results are given in Table 1 and are also shown graphically in Figure 1 (squares). The slopes of the plots of [unrearranged product]/[rearranged products] vs [amine] yield $k_{\mathrm{NH(D)}}^{373\mathrm{K}}/k_{\mathrm{r}}^{373\mathrm{K}}$. The value found for diphenylamine and N-deuteriodiphenylamine, viz., 30 and 13, respectively (see final column in Table 1), yield a deuterium kinetic isotope effect for reaction 9 of 30/13 = 2.3.

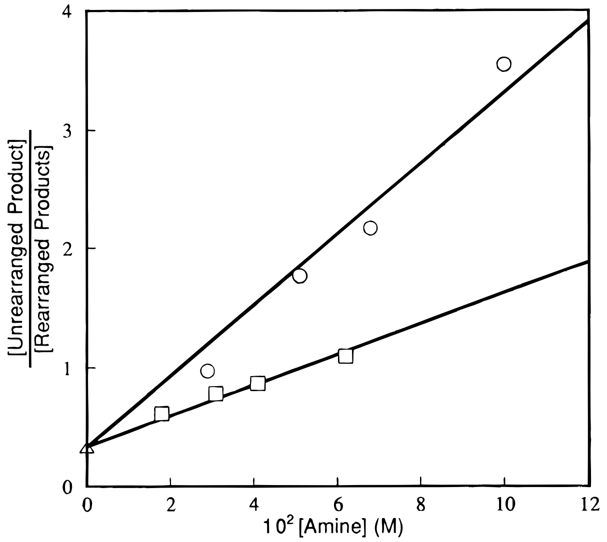

Figure 1. Plot according to eq I. Key: $\mathrm{Ph_2NH}$, ○; $\mathrm{Ph_2ND}$, □; at [amine] = 0, product ratio = 0.33, △.

A generally more limited set of experiments was carried out with four 4,4′-disubstituted diphenylamines. The substituents were bromine, methyl, methoxyl, and (mostly) *tert*, *tert*-octyl (2-neopentylpropane), the last being a commercial material, Naugalube 438L. The results of these experiments are listed in Table 1 together with the values calculated for $k_{\mathrm{NH(D)}}^{373\mathrm{K}}/k_{\mathrm{r}}^{373\mathrm{K}}$.

Discussion

The original, EPR-measured, Arrhenius parameters for the neophyl radical clock[12] (reaction 10) have been revised by Franz *et al.*[13] as a result of a careful study of the n-$\mathrm{Bu_3SnH}$/neophyl chloride reaction. The Arrhenius parameters given by Franz *et al.*[13] for this rearrangement (viz., $\log(A/\mathrm{s}^{-1}) = 11.5$, $E = 11.82$ kcal/mol) were based on the assumption that the neophyl radical would react with n-$\mathrm{Bu_3SnH}$ at the same rate as that measured for n-alkyl radicals.[14] However, it would appear that the Arrhenius parameters for reaction of the neopentyl radical with n-$\mathrm{Bu_3SnH}$ are slightly different from those for an n-alkyl radical.[15] Fortunately, the revised[13] and the "corrected" Arrhenius parameters for the neophyl rearrangement, viz.,

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(8) The absence of esters can be attributed to the short lifetime of the peroxide at 100 °C[9] and, in most experiments, the presence of an effective trap for the carbon-centered radicals which might otherwise have yielded esters and started a chain reaction.

(9) Primary aryl peroxides have $k \approx 10^{-2} - 10^{-3}\ \mathrm{s}^{-1}$ at 100 °C. See: Hiatt, R. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. 2, Chapter 8.

(10) The experimental points show some unexpected curvature which might be due to analytical errors or to a less than complete reaction scheme.

(11) Made by exchange of $\mathrm{Ph_2NH}$ in dodecane with a large excess of $\mathrm{D_2O}$ and subsequently including a small quantity of $\mathrm{D_2O}$ in each reaction vial. See: Howard, J. A.; Ingold, K. U. *Can J. Chem.* **1962**, *40*, 1851−1864.

(12) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224−1226, 4692.

(13) Franz, J. A.; Barrows, R. D.; Camaioni, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 3964−3967.

(14) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739−7742.

(15) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594−4596.

Table 1. Relative Yields of Products Arising from the Thermal Decomposition of 3-Methyl-3-Phenylbutanoyl Peroxide in Dodecane at 100 °C in the Absence and Presence of Some Diphenylamines

amine (10^2 M)	$PhCMe_3$	$PhCH_2CHMe_2$	$PhCH{=}CMe_2$	[unrearranged prod]/[rearranged prod][a]	$k^{373K}_{NH(D)}/k^{373K}_{r}$ [b] (M^{-1})
none[c]	0.80	(1.0)	1.42	0.33	
$(C_6H_5)_2NH$					
2.9	2.56	(1.0)	1.64	0.97	
5.1	5.72	(1.0)	2.24	1.77	
6.8	7.48	(1.0)	2.45	2.17	
10	17.8	(1.0)	4.02	3.55	30
$(C_6H_5)_2ND$					
1.8	1.05[d]	(1.0)	0.71	0.61	
3.1	1.61[d]	(1.0)	1.06	0.78	
4.1	1.96[d]	(1.0)	1.26	0.87	
6.2	2.67[d]	(1.0)	1.44	1.09	13
$(4\text{-}BrC_6H_4)_2NH$					
2.3	2.20	(1.0)	3.78	0.46	
4.0	2.59	(1.0)	4.22	0.50	
5.4	3.73	(1.0)	5.28	0.59	
8.1	5.71	(1.0)	8.26	0.62	3.9
$(4\text{-}MeC_6H_4)_2NH$					
2.2	3.35	(1.0)	1.34	1.43	
3.9	5.50	(1.0)	1.40	2.29	
5.2	8.00	(1.0)	1.48	3.23	53
$(4\text{-}MeOC_6H_4)_2NH$					
2.6	2.65	(1.0)	1.27	1.17	
3.4	7.33	(1.0)	1.96	2.48	
5.1	30.1	(1.0)	7.92	3.37	57
$(4\text{-}C_8H_{17}C_6H_4)_2NH$[e]					
4.1	6.47	(1.0)	1.07	3.13	
5.5	8.04	(1.0)	1.19	3.67	
8.2	8.93	(1.0)	0.80	4.96	59

[a] $[PhCMe_3]/[PhCH_2CHMe_2] + [PhCH{=}CMe_2]$. [b] Slope of the plot of [unrearranged product]/[rearranged products] vs [amine]. [c] Mean of five separate measurements. [d] $[PhCMe_2CH_2D]/[PhCMe_3] = 0.50$, 0.53, 0.56, and 0.83 as $(C_6H_5)_2ND$ changes from 1.8×10^{-2} to 6.2×10^{-2} M. [e] Mixture of isomeric octyl groups, see text.

$$\log(k_r/s^{-1}) = 10.98 - 10.83/\theta \qquad \text{(II)}$$

where $\theta = 2.3RT$ kcal/mol, yield essentially the same rate constant for the rearrangement at 100 °C. That is, equation II yields $k_r^{373K} = 4.3 \times 10^4\ s^{-1}$, whereas Franz *et al.*'s[13] parameters yield $k_r^{373K} = 3.8 \times 10^4\ s^{-1}$. Thus, the overall rate constant for hydrogen abstraction from dodecane by a primary alkyl radical at 100 °C is

$$k_{CH}^{373K} = 0.33 \times 4.3 \times 10^4/[C_{12}H_{26}]\ M^{-1}\ s^{-1} \qquad \text{(III)}$$

where $[C_{12}H_{26}]$ is the molar concentration of neat dodecane at this temperature which we estimate[16] to be 4.05 M. That is,

$$k_{CH}^{373K} = 1.42 \times 10^4/4.05 = 3.5 \times 10^3\ M^{-1}\ s^{-1} \qquad \text{(IV)}$$

Since hydrogen abstraction must occur predominantly at the alkane's 10 methylene groups, we obtain

$$k_{CH}^{373K}/(CH_2) = 3.5 \times 10^2\ M^{-1}\ s^{-1} \qquad \text{(V)}$$

Unfortunately, there would appear to be no data in the literature with which the present value of k_{CH}^{373K}/CH_2 might be compared.[17]

To obtain slightly more information about reaction 10, five additional experiments were carried out in the absence of amine at 80 °C and another five at 60 °C. The mean rate constant ratios were as follows: $(k_{CH}/k_r)^{353K} = 0.51/[C_{12}H_{26}]\ M^{-1}$ and $(k_{CH}/k_r)^{333K} = 0.60/[C_{12}H_{26}]\ M^{-1}$. Using the correct dodecane molarities at each temperature[16] and the k_r values derived from eq II, we obtain $k_{CH}^{353K} = 2.3 \times 10^3\ M^{-1}\ s^{-1}$ and $k_{CH}^{333K} = 1.0_5 \times 10^3\ M^{-1}\ s^{-1}$. Although rate constants measured at three temperatures covering such a small temperature range cannot yield reliable Arrhenius parameters, the "best" line through our three points gives,

$$\log(k_{CH}/M^{-1}\ s^{-1}) = 7.1 - 6.1/\theta \qquad \text{(VI)}$$

where error limits are not given (for obvious reasons). The expected pre-exponential factor for this class of reactions is $10^{8.5\pm0.5}\ M^{-1}\ s^{-1}$.[18]

Hydrogen atom abstraction from diphenylamine is, as would be expected, very much faster than abstraction from dodecane, i.e.,

$$(k_{NH}^{373K})_{Ph_2NH} = 30 \times 4.3 \times 10^4 = 1.3 \times 10^6\ M^{-1}\ s^{-1} \qquad \text{(VII)}$$

Experiments at 80 and 60 °C with four different concentrations of diphenylamine in each case yielded $k_{NH}/k_r = 38\ M^{-1}$ and $43\ M^{-1}$, respectively. Hence, via eq II, $(k_{NH}^{353K})_{Ph_2NH} = 7.2 \times 10^5\ M^{-1}\ s^{-1}$ and $(k_{NH}^{333K})_{Ph_2NH} = 3.2 \times 10^5\ M^{-1}\ s^{-1}$. Once again, these data are not expected to yield reliable Arrhenius parameters. The "best" line gives,

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(16) Densities for dodecane were obtained from Table 20d in: *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds;* Rossini, F. D., Ed.; Carnegie Press: Pittsburgh, PA, 1953. These densities are 0.6900, 0.7048, and 0.7198 g/mL at 100, 80, and 60 °C, respectively, corresponding to dodecane molarities of 4.05, 4.14, and 4.23 M at these three temperatures. We thank a reviewer for steering us to this data source.

(17) There are no kinetic data for any similar reaction in solution listed by: Lorand, J. P. In *Landolt Börnstein, New Series; Radical Reaction Rates in Solution;* Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13a, Chapter 2.

(18) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience : New York, 1976.

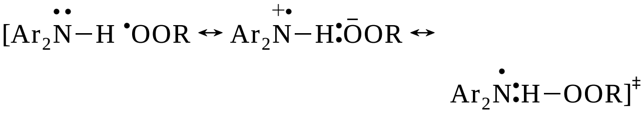
$$\log (k_{\mathrm{NH}})_{\mathrm{Ph_2NH}} = 11.2 - 8.6/\theta \qquad \text{(VIII)}$$

which has a preexponential factor well outside the "normal" range.[18] If the preexponential factor is assigned the (probably) more reasonable value of $10^{8.5}$ M^{-1} s^{-1} the activation energy would be ca. 4.1 kcal/mol.

Despite our uncertainties regarding the true temperature dependence of reaction 9, there can be no doubt that this reaction has a substantial activation energy. Furthermore, hydrogen abstraction from diphenylamine by a primary alkyl radical is certainly fast at temperatures ranging from 60 °C ($k_{\mathrm{NH}}^{333\mathrm{K}} \approx 3 \times 10^5$ M^{-1} s^{-1}) to 100 °C ($k_{\mathrm{NH}}^{373\mathrm{K}} \approx 1.3 \times 10^6$ M^{-1} s^{-1}). For comparison, rate constants for hydrogen abstraction from diphenylamine by peroxyl radicals, reaction 4, have been reported as $(k_4^{338\mathrm{K}})_{\mathrm{Ph_2NH}} = 4 \times 10^4$ M^{-1} s^{-1} [5] and $(k_4^{333\mathrm{K}})_{\mathrm{Ph_2NH}}$ 4.4×10^4 M^{-1} s^{-1}.[6] Thus, these peroxyl radical reactions are *slower* than hydrogen abstraction by primary alkyl radicals. There is also excellent experimental evidence indicating that the preexponential factors and activation energies for reaction 4 are unusually low.[19] Thus, hydrogen abstraction from aromatic amine antioxidants by alkyl radicals is certainly competitive with, and may frequently dominate, abstraction by peroxyl radicals at the elevated temperatures encountered in many practical situations, particularly in the case of gas turbine lubricant oils in jet aircraft operating at high altitudes (and hence at low oxygen pressures, see reaction 2). The fact that reaction 9 is faster than reaction 4 can be attributed to the greater exothermicity of the former reaction (ca. ~12 kcal/mol for a primary alkyl radical).

The deuterium kinetic isotope effect $(k_{\mathrm{NH}}^{373\mathrm{K}})_{\mathrm{Ph_2NH}}/(k_{\mathrm{ND}}^{373\mathrm{K}})_{\mathrm{Ph_2NH}} = 2.3$ (*vide supra*) which may be compared with $(k_4^{338\mathrm{K}})_{\mathrm{Ph_2NH}}/(k_4^{338\mathrm{K}})_{\mathrm{Ph_2ND}} = 3.0$ for hydrogen abstraction by peroxyl radicals.[5a] Analyses of the deuterium content of tert- and isobutylbenzene gave results consistent with Scheme 2. That is, all the isobutylbenzene contained one atom of deuterium (reaction 12) in each experiment but not all of the *tert*-butylbenzene contained one deuterium (see footnote *d* of Table 1).[21]

The data for the 4,4′-disubstituted diphenylamines (see Table 1) reveal a significant polar effect on reaction 9. Two electron-withdrawing *p*-bromine atoms (σ/Br = +0.26)[22] reduce ($k_{\mathrm{NH}}^{373\mathrm{K}}$) by a factor of 7.7 relative to the unsubstituted amine, and two electron-releasing methyl (σ/Me = −0.14),[22] methoxyl (σ/MeO = −0.12),[22] and *tert*,*tert*-octyl ($\sigma/\mathrm{Me_3C} = -0.15$)[22] groups increase $k_{\mathrm{NH}}^{373\mathrm{K}}$ by slightly less than a factor of 2. A Hammett plot of log ($k_{\mathrm{NH}}^{373\mathrm{K}}/M^{-1}$ s^{-1}) against $\Sigma\sigma$ yields a reasonable correlation with $\rho \approx -1.4$. For comparison, the logarithm of the rate constants for hydrogen abstraction from 3- or 4-substituted and 4,4′-disubstituted diphenylamines by peroxyl radicals at 65 °C were very much better correlated by $\Sigma\sigma^+$ ($\rho^+ = -0.89$) than by $\Sigma\sigma$.[5b] The correlation of the rates of hydrogen abstraction by electrophilic peroxyl radicals with $\Sigma\sigma^+$ is readily understood in terms of polar contributions to the transition state, i.e.



$$[\mathrm{Ar_2}\overset{\bullet\bullet}{\mathrm{N}}\!-\!\mathrm{H}\ {}^{\bullet}\mathrm{OOR} \leftrightarrow \mathrm{Ar_2}\overset{+\bullet}{\mathrm{N}}\!-\!\mathrm{H}{:}\bar{\mathrm{O}}\mathrm{OR} \leftrightarrow \mathrm{Ar_2}\overset{\bullet}{\mathrm{N}}{:}\mathrm{H}\!-\!\mathrm{OOR}]^{\ddagger}$$

Such transition state stabilization is not available for abstractions by primary alkyl radicals which are neither strongly electrophilic nor strongly nucleophilic.[23]

Conclusion

Hydrogen atom abstraction from diarylamine antioxidants by carbon-centered radicals is a reaction which cannot be ignored in kinetic modeling studies of inhibited hydrocarbon autoxidations at elevated temperatures, particularly at oxygen pressures less than those existing at sea level.[24]

Experimental Section

Materials. The 4,4′-disubstituted diphenylamines were synthesized by literature procedures from readily available commercial materials and had physical properties which agreed with literature reports.

4,4′-Dibromodiphenylamine.[27] Diphenylamine + benzoyl chloride → *N*-benzoyldiphenylamine + Br_2 → dibromodiphenylamine (mp 104−6 °C (lit.[27] mp 105.5−7 °C); ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.6 (1H, s), 6.8 (4H, d, J = 10 Hz), 7.3 (4H, d, J = 10 Hz)).

4,4′-Dimethyldiphenylamine.[27] 4-Methylaniline + acetic anhydride → *N*-acetyl-4-methylaniline + 4-bromotoluene → dimethyldiphenylamine (mp 75−6 °C (lit.[27] mp 82−83 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.2 (1H, s), 3.0 (6H, s), 7.7 (8H, m)).

4,4′-Dimethoxydiphenylamine.[27] 4-Methoxyaniline + acetic anhydride → *N*-acetyl-4-methoxyaniline + 4-bromoanisole → dimethoxydiphenylamine (mp 99−100 °C (lit.[27] mp 100−102 °C); ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.9 (7H, s), 7.0 (8H, m)).

***N*-Deuteriodiphenylamine** was prepared from triply recrystallized diphenylamine (0.21 g, 1.24 mmol) in *n*-dodecane (10 mL) to which was added 99.8% D_2O (5 mL), and the liquids were stirred for 1 h. For the kinetic runs, aliquots of the dodecane solution were removed together with some D_2O to ensure that dedeuteration by adventitious H_2O did not occur.

3-Methyl-3-phenylbutanoyl peroxide was synthesized from neophyl chloride via 3-methyl-3-phenylbutanoic acid. Neophyl chloride (21 g, 0.125 mol) and magnesium turnings (3.2 g, 0.13 mol) in dry ether (100 mL) were refluxed for 10 h under a dry N_2 atmosphere, following which dry CO_2 was bubbled through the mixture for 5 h. Acidification (dilute HCl), extraction with ether (3 × 100 mL), and removal of most of the ether was followed by addition of 5 M NaOH (200 mL).

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(19) For example:[20] amine, log (A/M^{-1} s^{-1}), E (kcal/mol): α-naphthylamine, 3.9, 1.0; phenyl-α-naphthylamine, 5.1, 1.0; β-naphthylamine, 5.0, 2.3; aniline, 6.6, 5.0.

(20) Howard, J. A.; Furimsky, E. *Can. J. Chem.* **1973**, *51*, 3738−3745. Chenier, J. H. B.; Furimsky, E.; Howard, J. A. *Can. J. Chem.* **1974**, *52*, 3682−3688.

(21) At first sight it appeared that it would be possible to calculate $k_{\mathrm{ND}}^{373\mathrm{K}}/k_{\mathrm{CH}}^{373\mathrm{K}}$ from these data since a simple kinetic analysis *which ignores reaction 13* yields: $k_{\mathrm{ND}}^{373\mathrm{K}}/k_{\mathrm{CH}}^{373\mathrm{K}} = ([\mathrm{PhCMe_2CH_2D}]/[\mathrm{PhCMe_3}])([\mathrm{C_{12}H_{26}}]/[(\mathrm{C_6H_5})_2\mathrm{ND}])$. However, with $[\mathrm{C_{12}H_{26}}] = 4.05$ M and $k_{\mathrm{CH}}^{373\mathrm{K}} = 3.5 \times 10^3$ M^{-1} s^{-1}, the values calculated for $k_{\mathrm{ND}}^{373\mathrm{K}}$ range from 1.9×10^5 M^{-1} s^{-1} to 3.9×10^5 M^{-1} s^{-1}. Such values are considerably smaller than the value which can be calculated for $(k_{\mathrm{ND}}^{373\mathrm{K}})_{\mathrm{Ph_2ND}}$ from the data in Table 1, viz. 5.6×10^5 M^{-1} s^{-1}. We attribute the lower than "expected" $[\mathrm{PhCMe_2CH_2D}]/[\mathrm{PhCMe_3}]$ ratios to reaction 13, $X^{\bullet} = \mathrm{PhCMe_2CH_2}^{\bullet}$.

(22) Exner, O. In *Conformational Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; Chapter 10.

(23) Certainly this appears to be true for methyl radicals. See: Wong, M. W.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 11050−11051.

(24) Hydrogen atom abstraction from the very good phenolic antioxidant α-tocopherol (vitamin E) by a primary alkyl radical is also a rapid reaction, $k^{343\mathrm{K}} = 1.7 \times 10^6$ M^{-1} s^{-1} in benzene.[25] As would be expected, less effective phenolic antioxidants would appear to be less reactive to carbon-centered radicals, e.g.,[26] $k^{298\mathrm{K}}(\mathrm{Me_3C^{\bullet}} + \mathrm{PhOH}) = 14$ M^{-1} s^{-1}, $k^{298\mathrm{K}}(\mathrm{Me_3C^{\bullet}} + 2,6\text{-}(\mathrm{Me_3C})_2\mathrm{C_6H_3OH}) = 93$ M^{-1} s^{-1}.

(25) Evans, C.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4589−4593.

(26) Ruegge, D.; Fischer, H. *Int. J. Chem. Kinet.* **1989**, *21*, 703−714.

(27) Chen, M. M.; D'Adamo, F. A.; Walter, R. I. *J. Org. Chem.* **1961**, *26*, 2721−2727.

The resulting aqueous solution was washed with ether (3 × 70 mL) and then acidified, and the 3-methyl-3-phenylbutanoic acid was extracted with ether (yield 11.4 g, 50%; mp 55 °C lit.[28] mp 56−7 °C); ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.5, 149.0, 128.7, 126.5, 125.9, 48.5, 36.0, 28.9; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.2−7.5 (5H, m), 2.65 (2H, s), 1.5 (6H, s)). This acid (1.78 g, 10 mmol) was dissolved in dry ether (20 mL), and oxalyl chloride (3 g, 24 mmol) was added slowly (anhydrous conditions in an ice bath). After the solution was refluxed for 2 h, the solvent and excess oxalyl chloride were removed under vacuum. The resulting clear liquid plus 20 mL of ether was cooled in an ice bath, and hydrogen peroxide (0.62 g of 27.5% aqueous solution, 5 mmol H_2O_2) and pyridine (1 g, 13 mmol) were added with stirring for 2 h at temperatures below 2 °C. The product was washed first with dilute HCl and then with saturated Na_2CO_3 followed by drying over anhydrous Na_2SO_4. No attempt was made to concentrate all the product to record a yield for fear of its decomposition. However, a portion was evaporated to obtain NMR spectra on the crude product: ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.2, 149.0, 128.7, 126.5, 125,9, 44.4, 36.0, 28.9; ^{1}H NMR (200 Mz, $CDCl_3$) δ 7.2−7.5 (5H, m), 2.7 (2H, s), 1.5 (6H, s).

Experimental Procedure. *n*-Dodecane was passed through alumina prior to use. Standard solutions of the amine and the peroxide were made up in this solvent. Aliquots of the amine and peroxide solutions were further diluted with dodecane in glass vials which were degassed by freeze, pump, thaw cycles and were then sealed under a few Torr of N_2. Reactions were carried out five at a time in a Pye-Unicam GC oven with the samples generally being left in the oven for sufficient time (up to a few days) to ensure complete reaction. The relative yields of the three hydrocarbon products were determined (using authentic standards) by GC (5 m, OV 101 at 10% loading, N_2 carrier gas, 95 °C, FID). Retention times were ca. 1 h, and the column required N_2 purging for 1 h at 250 °C after each analysis.

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[28] Bordwell, F. G.; Almy, J. *J. Org. Chem.* **1973**, *38*, 575−579.