Reactivity and Structure of *N*-Phenylnaphth-1-ylamines and Related Compounds. Part 1. Reactions with Alkylperoxyl Radicals

John E. Bennett and George Brunton
Shell Research Ltd., Thornton Research Centre, P.O. Box 1, Chester CH1 3SH
Alexander R. Forrester* and Joseph D. Fullerton
Chemistry Department, University of Aberdeen, Old Aberdeen AB9 2UE

Rate constants for the reaction of a series of *N*-phenylnaphth-1-ylamines and some related nitroxides and hydroxylamines with t-alkylperoxyl radicals have been measured using kinetic e.s.r. spectrometry and activation energies and *A* factors have been derived. The stoicheiometry of the reaction (peroxyl radical to *N*-phenylnaphth-1-ylamine) has been shown to be *ca.* 2 in all cases.

Aromatic amines (AH) are used as antioxidants to protect organic materials against atmospheric oxidation.[1-3] They react with chain-propagating alkylperoxyl radicals (ROO·) by rapid intermolecular hydrogen exchange (i) to form a free radical (A·) which does not propagate the chain.

$$ROO^{\bullet} + AH \xrightarrow{k_1} ROOH + A^{\bullet} \qquad \text{(i)}$$

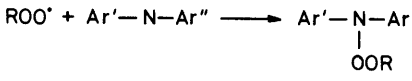
The subsequent reactions of the aminyl (A·) can be varied and lead to a complex product distribution. Reaction with a second peroxyl radical can occur either at the nitrogen (ii) or at the aromatic ring (iii). In either case subsequent reaction occurs to give radical (iv) or molecular (v) products. High yields of the nitroxide, which have been observed for substituted diphenylamines,[4] indicate that reaction (ii) at nitrogen is a major reaction pathway for these amines. On the other hand low yields of nitroxides, which are found from *N*-phenylnaphthylamines,[4,5] have been taken as evidence for preferential ring addition (iii). This conclusion is supported by the detection of oxygenated products such as quinone imines and their derivatives.[5] However, low yields do not necessarily exclude reaction *via* the nitroxide if the subsequent reactions are fast. Furthermore, the product distributions can be accounted for in terms of reactions of quinone imine *N*-oxides formed by reaction of peroxyl radicals with the nitroxide.

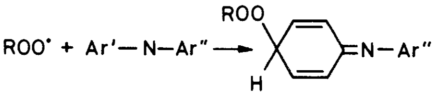
Because of the complexity of the subsequent reactions there are few reliable measurements of the kinetics of the primary inhibition step [reaction (i)] for amines. From oxidation experiments rate constants have been obtained at a single temperature (338 K) for the reactions of the polystyrylperoxyl radical with a range of amines.[6,7] Rate constants over a temperature range (176—238 K) have been obtained directly for the reactions of t-butylperoxyl radicals with naphth-1-ylamine and *N*-phenylnaphth-1-ylamine by using kinetic e.s.r. spectroscopy.[8]

We have carried out kinetic, spectroscopic, and product studies of the reactions of a series of substituted *N*-phenyl naphth-1-ylamines with peroxyl radicals and hydroperoxides to gain a better understanding of the antioxidant behaviour of these compounds. In this paper we describe the kinetic results for reactions of an alkylperoxyl radical with the amines, some of the corresponding nitroxides, and related compounds. Product studies will be reported subsequently.

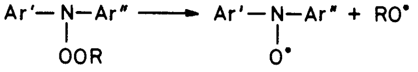
Experimental

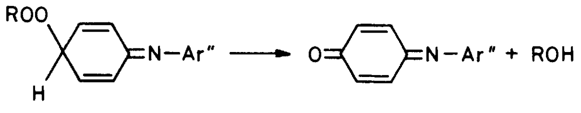
Materials.—*N*-Phenylnaphth-1-ylamine was obtained commercially. The preparation of the amines (4)—(7) and nitroxides (10)—(12) will be reported elsewhere. Details of the amines (8) and (13) and hydroxylamines (9) and (14) have been reported previously.[9,10]


$$ROO^{\bullet} + Ar'{-}N{-}Ar'' \longrightarrow Ar'{-}\underset{OOR}{N}{-}Ar''$$
(ii)


(iii)

(when Ar' = Ph)


$$Ar'{-}\underset{OOR}{N}{-}Ar'' \longrightarrow Ar'{-}\underset{O^{\bullet}}{N}{-}Ar'' + RO^{\bullet}$$
(iv)

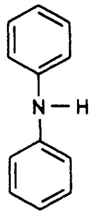

(v)

Kinetic E.s.r. Spectrometry.—The experimental method entails the combination of rapid-recording e.s.r. spectrometry and flash photolysis. The peroxyl radicals were formed photolytically from suitable precursors (see below) and their decay in the presence of a large excess of the amine was monitored by e.s.r. spectrometry.

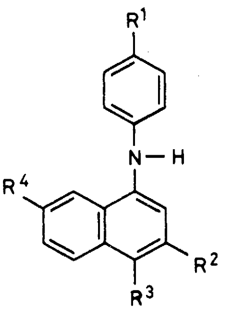
The flash lamp was an ILC 5Fl xenon-filled lamp (5 mm bore, 25 mm arc length) and was run at 30 J per flash (input electrical energy) from an ILC PS 150 discharge system. The lamp was cooled by passing a current of air through a fused silica tube surrounding it. The light output was coupled into the sample cavity of the e.s.r. spectrometer by a fused silica light pipe (Schott QLT, 300 mm long, 10 mm diameter).

The e.s.r. measurements were made with a Varian Century E-109 spectrometer and accessories. The signal from the unfiltered output was fed into a Biomac 1 000 signal averager (1 000 channels, minimum read-in time 5 μs per channel). To obtain an accurate base line for the decay curves, the flash lamp was triggered by a pulse from the signal averager when it had reached channel 64. A suitable delay (minimum 320 ms) between successive sweeps ensured that the radical concentration had decayed to zero before the next flash. To obtain a reasonable signal-to-noise ratio a number (usually 64, but occasionally up to 256) of separate decay curves were averaged for each measurement.

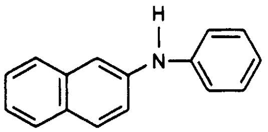
The sample temperatures were controlled by a standard Varian variable-temperature accessory. The actual sample temperature was measured with a copper–constantan thermocouple immediately after each experiment.



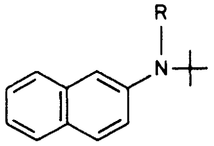
(1)



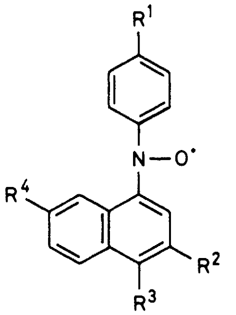
(2) $R^1 = R^2 = R^3 = R^4 = H$
(4) $R^1 = Bu^t, R^2 = R^3 = R^4 = H$
(5) $R^1 = R^2 = R^4 = Bu^t, R^3 = H$
(6) $R^1 = R^3 = H, R^2 = R^4 = Bu^t$
(7) $R^1 = R^3 = Bu^t, R^2 = R^4 = H$



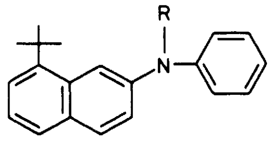
(3)



(8) R = H
(9) R = OH



(10) $R^1 = Bu^t, R^2 = R^3 = R^4 = H$
(11) $R^1 = R^2 = R^4 = Bu^t, R^3 = H$
(12) $R^1 = R^3 = Bu^t, R^2 = R^4 = H$



(13) R = H
(14) R = OH

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\bullet \qquad \text{(vi)}$$

$$Bu^tO^\bullet + ROOH \longrightarrow Bu^tOH + ROO^\bullet \qquad \text{(vii)}$$

$$ROO^\bullet + A^\bullet \xrightarrow{\text{fast}} \text{products} \qquad \text{(viii)}$$

The peroxyl radical (1-methylcyclohexylperoxyl) was generated by photolysis of a solution of di-t-butyl peroxide 4% v/v) and 1-methylcyclohexyl hydroperoxide (1% v/v) in toluene. 1-Methylcyclohexylperoxyl radical was chosen in preference to t-butylperoxyl radical in order to reduce the effects of line broadening at higher temperatures.[11] The increase in linewidth with increasing temperature is very marked for peroxyl radicals owing to the strong spin–rotation interaction.[12] This effect is less in the more bulky 1-methylcyclohexylperoxyl radical than for the approximately spherical t-butylperoxyl radical. In general the upper temperature limit for kinetic measurements with peroxyl radicals is determined by the loss in sensitivity caused by this line broadening rather than by the increasing rate of reaction.

Approximately 10^{-6} mol l^{-1} of peroxyl radicals were formed per flash, while the amines were present in the solution at *ca.* 10^{-3} mol l^{-1}. The solutions were prepared immediately before the experiment by mixing equal volumes of a solution containing the peroxides and a solution of the amine.

Stoicheiometric Measurements.—The stoicheiometry of the reaction between the peroxyl radicals and several of the amines was measured using the technique described by Chenier *et al.*[13] Briefly a steady concentration of t-butylperoxyl radicals was generated by photolysis of a solution of di-t-butyl peroxide and t-butyl hydroperoxide in a toluene–pentane solution at 178 K in the cavity of the e.s.r. spectrometer. Then a known quantity of the amine (which was significantly less than the stoicheiometric amount) was added slowly and the decrease in the intensity of the peroxyl radical signal was measured. The measurements were calibrated by comparison with the decrease in intensity for a standard amine (in this case *N*-phenylnaphth-1-ylamine for which the stoicheiometry has been measured previously;[8] peroxyl : amine = 2).

Results

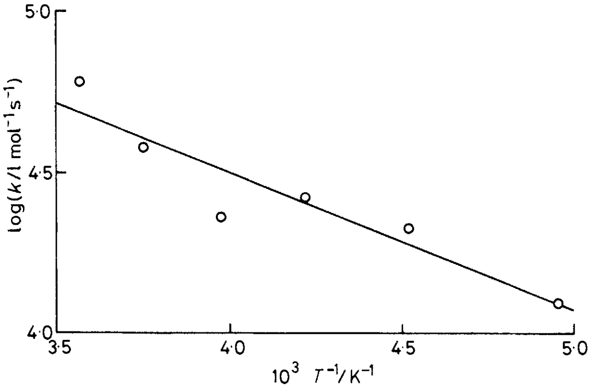
Kinetic Measurements.—From the earlier measurements by Howard and Furimsky[8] and our results (see below) the stoicheiometry for the reaction with all the amines examined is close to 2. Thus reaction (i) must be followed rapidly by reaction with a second peroxyl radical to give products which are relatively unreactive towards peroxyl radicals [reaction (viii)].

The rate of disappearance of ROO· is given by $d[ROO\cdot]/dt = 2k_1[ROO\cdot][AH]$. Thus in the presence of a large excess of amine the decay of peroxyl radicals was pseudo-first order

Table 1. Arrhenius parameters and rate constants for amines, nitroxides, and hydroxylamines

Amine/nitroxide	E_1/kJ mol^{-1} [a]	log (A/l mol^{-1} s^{-1}) [a]	k_1 (253 K)/l mol^{-1} s^{-1}	k_1 (338 K)/l mol^{-1} s^{-1}	k_1 (autox)/l mol^{-1} s^{-1} [b]
(1) [c]	6.5 ± 0.5	4.66 ± 0.09		4.6×10^3	2.0×10^4
(2)	11.0 ± 2.0	6.05 ± 0.35		2.2×10^4	3.5×10^4
(3) [c]	9.5 ± 1.2	5.38 ± 0.32		8.5×10^3	2.5×10^4
(4)	14.6 ± 2.5	7.74 ± 0.54	5.5×10^4	3.1×10^5	
(5)	13.9 ± 2.6	7.71 ± 0.51	7.3×10^4	3.8×10^5	
(6)	11.1 ± 2.9	7.26 ± 0.61	9.6×10^4	3.6×10^5	
(7)	8.3 ± 1.5	6.23 ± 0.34	3.4×10^4	9.1×10^4	
(8)	7.2 ± 1.2	4.28 ± 0.23	6.1×10^2	1.5×10^3	
(9)	4.6 ± 0.9	5.44 ± 0.18	3.3×10^4	5.8×10^4	
(10)			3.4×10^3		
(11)			3.3×10^3		
(12)			1.4×10^3		

[a] Root mean square errors. [b] Results at 338 K from refs. 6 and 7 (recalculated, see text). [c] Results from ref. 14.



Arrhenius plot for naphth-1-ylamine (7)

with the measured rate constant, k_m, given by $k_m = 2k_1[AH]$. (All the kinetic parameters for the naphthylamines were calculated on this basis.) The amines (4)—(8) and (13), hydroxylamines (9) and (14), and nitroxides (10)—(12) were used for the kinetic and other measurements.

Kinetic measurements were made over as wide a range of temperature as possible, generally commencing at *ca.* 200 K and increasing in temperature until the signal : noise ratio had deteriorated to an unacceptable level. A typical Arrhenius plot is shown in the Figure. The activation energies (E_1), A factors (A_1), and values of the rate constants at 253 and 338 K are given in Table 1. For comparison we include results for the reaction with diphenylamine,[14] which have been calculated on the basis of a stoicheiometric factor of 1.

For all the naphthylamines there was little accumulation of the nitroxide radical during the kinetic experiments. In contrast relatively high concentrations of diphenyl nitroxide accumulated in the experiments with diphenylamine. To complement these observations a few experiments were carried out to measure the concentration of nitroxide produced during a thermally initiated oxidation of the amine (13) and the corresponding hydroxylamine (14). The procedure was similar to that used by Ingold and his co-workers.[4,15] The results are given in Table 2, together with relevant measurements from the earlier work. In all cases, except for diphenylamine, the maximum yield of nitroxide was relatively low.

Kinetic measurements using the nitroxides were difficult to obtain because of considerable overlap of their spectra with that of the peroxyl radical. Consequently results were obtained for a single temperature (253 K) and could not be measured with the same degree of accuracy as that for the amines.

Table 2. Nitroxide accumulation during thermally initiated autoxidation

Inhibitor	T/°C	10^4 [Inhibitor]/ mol l^{-1}	10^5 [Nitroxide]$_{max.}$/ mol l^{-1}	%
(1) [a]	65	8.3	19	23
(2) [a]	65	8.3	0.4	0.5
(3) [a]	65	8.3	0.4	0.5
(13)	102	5.16	2.2	4.26
(14)	103	4.95	3.1	6.16

[a] Ref. 4.

Table 3. Relative stoicheiometry of reaction of *N*-phenylnaphth-1-ylamines with t-butylperoxyl radicals

Amine	Amine : Bu^{t}OO·
(2)	2
(4)	1.66
(5)	1.86
(6)	1.88
(7)	2.74

Stoicheiometric Measurements.—The experiments proved to be difficult to carry out and the overall accuracy was not high. The results for the five compounds examined in this way are given in Table 3. The values for amines (4)—(6) were close to 2 as found previously[8] for the unsubstituted *N*-phenylnaphth-1-ylamine. However, the value for amine (7) appears to be significantly higher and may indicate that the subsequent reaction pathway is different (product studies also support this inference).

Discussion

Within the accuracy of the results the activation energies (E_1) for the hydrogen abstraction are similar for all the amines studied. The low values are comparable to those found for a range of hindered phenols[8] and probably indicate that the reaction occurs *via* a hydrogen-bonded complex similar to that postulated for the phenols. However, our values of E_1 and A_1 for amine (2) are significantly higher than those [E_1 4.2 kJ mol^{-1}, log (A l mol^{-1} s^{-1}) 5.1] reported by Howard and Furimsky[8] for the reaction with t-butylperoxyl radicals. A similar observation has been made with the hindered phenols. Experiments show that the different structure of the peroxyl radicals has negligible effect. At present we do not have a satisfactory explanation for the difference, but it appears to be due partly to the different solvent systems used.[16]

N-Phenylnaphth-2-ylamine (3) appears to be slightly less reactive than *N*-phenylnaphth-1-ylamine and, as expected, the *N*-alkylnaphth-2-ylamine (8) is even less reactive towards hydrogen abstraction by peroxyl radicals. In contrast the rate constants for the corresponding hydroxylamine (9) are markedly greater than those for the amine. Further the activation energy for the reaction with the hydroxylamine (9) is less than that for the amine (8). These observations are in accord with the lower bond strength of N–OH (291 kJ mol^{-1}) [17] compared with that of N–H (335 kJ mol^{-1}).[18]

The presence of alkyl substituents on the rings increases the rate constant by a factor of *ca.* 5—15 [*cf.* amines (2) and (4)—(7)]. However, no trend with respect to the position or degree of substitution is evident from the present results. A similar enhancement has been observed previously in a series of substituted diphenylamines.[19]

A comparison may also be made with the rate constants obtained by Brownlie and Ingold [6,7] from the inhibited autoxidation of styrene at 338 K by extrapolating our results to this temperature. There is good agreement between the results for *N*-phenylnaphth-1-ylamine (2), but our values for diphenylamine and *N*-phenylnaphth-2-ylamine are somewhat lower than those obtained by the less direct method. However, in view of the probable errors in both sets of measurements the differences (factors of 3—4) are not excessive. [Brownlie and Ingold assumed a stoicheiometry of 1 for the reactions of peroxyl radicals with all three amines (1)—(3). In the light of our own results and those of Howard [8] we have adjusted the rate constants for the phenylnaphthylamines (2) and (3) using a stoicheiometric factor of 2.]

Turning next to the reaction of peroxyl radicals with the nitroxides it is evident that the rate constants are very much lower than for the corresponding amines [*cf.* (10) and (4); (11) and (5); (12) and (7)]. In fact these values may well be upper limits, because traces of the parent amine would lead to erroneously high rates. A similar trend [19] has been found for 4,4′-dimethoxydiphenyl nitroxide and the parent amine at 338 K, where the rate constant for the nitroxide is 0.15 times that of the amine.

Unlike diphenylamine the *N*-phenylnaphthylamines do not yield high concentrations of the corresponding nitroxides by reaction with photolytically generated peroxyl radicals or during a thermally initiated oxidation. This behaviour could be due either to little reaction occuring at the nitrogen of the aminyl [reaction (ii)] or to a very fast reaction of nitroxide once it is formed. Our kinetic results exclude the latter alternative as the nitroxide radicals are relatively unreactive towards peroxyl radicals. Surprisingly the maximum concentration of nitroxide obtained from the hydroxylamine (14) is not markedly greater than that from the corresponding amine (13), even though the nitroxide should be formed directly by hydrogen abstraction from the hydroxylamine. As the stoicheiometry of the reaction is close to 2 (peroxyl radicals per amine molecule) it appears that reaction with the aminyl radical must occur mainly by addition to the phenyl or naphthyl ring [reaction (iii)] and the formation of quinone imines. The product studies to be reported elsewhere lend support to this hypothesis.

References

1 L. R. Mahoney, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 547.
2 J. A. Howard, *Adv. Free-Radical Chem.*, 1972, **4**, 49.
3 K. U. Ingold, Chem. Soc. Special Publ., 1970, No. 24, p. 285.
4 K. Adamic and K. U. Ingold, *Can. J. Chem.*, 1969, **47**, 295.
5 D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, 1969, **34**, 3456.
6 I. T. Brownlie and K. U. Ingold, *Can. J. Chem.*, 1967, **45**, 2419.
7 I. T. Brownlie and K. U. Ingold, *Can. J. Chem.*, 1966, **44**, 861.
8 J. A. Howard and E. Furimsky, *Can. J. Chem.*, 1973, **51**, 3738.
9 A. Calder, A. R. Forrester, and G. McConnachie, *J. Chem. Soc., Perkin, Trans. 1*, 1974, 2198.
10 A. R. Forrester, S. P. Hepburn, and G. McConnachie, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2213.
11 J. E. Bennett and R. Summers, *J. Chem. Soc., Faraday Trans. 2*, 1973, 1043.
12 P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, 1966, **49**, 169.
13 J. H. B. Chenier, E. Furimsky, and J. A. Howard, *Can. J. Chem.*, 1974, **52**, 3682.
14 J. E. Bennett and S. Bahia, unpublished results.
15 K. Adamic, M. Dunn, and K. U. Ingold, *Can. J. Chem.*, 1969, **47**, 287.
16 J. E. Bennett, unpublished results.
17 K. U. Ingold, *J. Am. Chem. Soc.*, 1973, **95**, 8610.
18 E. T. Denisov, *Russ. Chem. Rev.*, 1973, **42**, 157.
19 I. T. Brownlie and K. U. Ingold, *Can. J. Chem.*, 1967, **45**, 2427.

Received 4th October 1982; *Paper* 2/1700