Kinetics of Inhibition of Hydrocarbon Autoxidation by 1,1′-Bis(*N*-phenyl-2-naphthylamine)

R. F. BRIDGER

Mobil Research and Development Corporation, Central Research Division Laboratory, Princeton, New Jersey 08540

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The kinetics of inhibition of cumene autoxidation at 60° by 1,1′-bis(*N*-phenyl-2-naphthylamine), a sterically hindered amine, are reported. The stoichiometry of inhibition indicates consumption of two peroxy radicals per amino group. The deuterium isotope effect $[k_5(\mathrm{H})/k_5(\mathrm{D})]$ is 3.6 in the rate-determining hydrogen transfer step. This hydrogen transfer is unusually slow ($k_5 = 1320\ M^{-1}\ \mathrm{sec}^{-1}$), and the kinetics suggest an abnormally fast reverse reaction. Experiments with inhibited autoxidations of tetralin indicate that the inhibitor radicals abstract hydrogen atoms from the hydrocarbon. The failure of steric hindrance about the amino group to reduce hydrogen abstraction reactions by inhibitor radicals stands in strong contrast to experience with hindered phenols.

1,1′-Bis(*N*-phenyl-2-naphthylamine) (bis-PBN) is formed by the coupling of amino radicals during oxidation of *N*-phenyl-2-naphthylamine (PBN).[1] As an oxidation inhibitor this compound is of interest for several reasons. Naphthylamines with substituents on the naphthyl moiety are not commonly used as antioxidants, and the effect of such substitution on the inhibition kinetics is unknown. Bis-PBN is formed as an intermediate[2] during inhibition by *N*-phenyl-2-naphthylamine and, as such, may be kinetically significant as a secondary inhibitor during high temperature antioxidation by PBN. Bis-PBN is one of the few examples of a highly hindered amine antioxidant. Ingold and coworkers have reported results for the highly hindered 2,4,6-tri-*tert*-butylaniline.[3] They have subsequently shown, however, that primary aromatic amines are anomalous in their behavior toward peroxy radicals[4] and are not representative of the diarylamines commonly used as antioxidants in practice.

Results and Discussion

Reactions which must be considered during the inhibition of hydrocarbon autoxidation are shown below,[5] where RH is hydrocarbon, $\mathrm{RO_2H}$ is hydroperoxide,

$$\mathrm{I} \xrightarrow{2ek_1} 2\mathrm{R}\cdot \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RO_2}\cdot \tag{2}$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{RO_2H} + \mathrm{R}\cdot \tag{3}$$

$$2\mathrm{RO_2}\cdot \xrightarrow{k_4} \mathrm{O_2} + \text{inert products} \tag{4}$$

$$\mathrm{RO_2}\cdot + \mathrm{AH} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{RO_2H} + \mathrm{A}\cdot \tag{5}$$

$$\mathrm{A}\cdot + \mathrm{RO_2}\cdot \xrightarrow{k_6} \text{inert products} \tag{6}$$

$$2\mathrm{A}\cdot \xrightarrow{k_7} \text{inert products} \tag{7}$$

$$\mathrm{A}\cdot + \mathrm{RH} \xrightarrow{k_8} \mathrm{AH} + \mathrm{R}\cdot \tag{8}$$

AH is the inhibitor, and I is the initiator, 2,2′-azobis(2-methylpropionitrile). Various kinetic expressions have been derived,[5-10] using all or part of eq 1-8. The apparent kinetic orders in [I], [RH], and [AH] generally indicate which reactions can be neglected. Rates of oxidation of tetralin at 60° inhibited by bis-PBN exhibited nonintegral kinetic orders in all reactants. The

$$-\frac{\mathrm{d[O_2]}}{\mathrm{d}t} = R_0 \propto \frac{[\mathrm{I}]^{0.8}[\mathrm{RH}]^{1.5}}{[\mathrm{AH}]^{0.7}}$$

three-halves order in tetralin is taken as a definite indication of hydrogen transfer from hydrocarbon to inhibitor radical (reaction 8).[8] Inhibited oxidations of cumene resulted in first-order dependence on hydrocarbon concentration. The nonintegral orders in [I]

$$R_0 \propto \frac{[\mathrm{I}]^{0.9}[\mathrm{RH}]^{1.0}}{[\mathrm{AH}]^{0.7}}$$

and [AH] suggest that reaction −5 is important. This was confirmed by an apparent kinetic order in hydroperoxide of about 0.5 (see below), indicating applicability of the following kinetic expression[6,7] in cumene.

$$R_0 = \frac{k_3[\mathrm{RH}]ek_1[\mathrm{I}]}{2k_5[\mathrm{AH}]}\left[1 + \left\{1 + \frac{4k_5k_{-5}[\mathrm{AH}][\mathrm{RO_2H}]}{k_6ek_1[\mathrm{I}]}\right\}^{1/2}\right] \tag{9}$$

Although cumene is not generally the hydrocarbon of choice because of its low value of k_3, it is well suited to the present study because k_8 vanishes, and k_5 is small enough that oxidation rates are large enough to measure conveniently.

The stoichiometry of inhibition and deuterium isotope effect were examined as criteria of normal antioxidant behavior. The stoichiometries of inhibition of bis-PBN and 1,1′-bis(di-2-naphthylamine) were determined by the inhibition period method,[11] with the results summarized in Table I. Each amine stopped four kinetic chains per molecule, equivalent to two peroxy radicals per amino group, as anticipated by the results of Thomas and Tolman with diphenylamine.[12]

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[1] (a) R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, **33**, 4329 (1968); (b) R. F. Bridger, *ibid.*, **35**, 1746 (1970).

[2] D. F. Bowman, B. S. Middleton, and K. U. Ingold, *ibid.*, **34**, 3456 (1969).

[3] D. V. Gardner, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **42**, 2847 (1964).

[4] K. Adamic and K. U. Ingold, *ibid.*, **47**, 295 (1969).

[5] L. R. Mahoney, *Angew. Chem., Int. Ed. Engl.*, **8**, 547 (1969); *J. Amer. Chem. Soc.*, **89**, 1895 (1967).

[6] J. R. Thomas, *ibid.*, **85**, 2166 (1963); **86**, 4807 (1964).

[7] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 2324, 2724 (1964).

[8] L. R. Mahoney and F. C. Ferris, *J. Amer. Chem. Soc.*, **85**, 2346 (1963).

[9] A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.* 2215 (1956); 2217 (1957).

[10] W. A. Waters and C. Wickham-Jones, *ibid.*, 812 (1951).

[11] C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Amer. Chem. Soc.*, **77**, 3233 (1955).

[12] J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2930 (1962).

TABLE I

STOICHIOMETRY OF INHIBITION OF 3.46 *M* CUMENE AUTOXIDATION AT 60°

Inhibitor,[a] 4 × 10^{-4} *M*	Initiator concn, *M*	t,[b] min	n[c]
1,1′-Bis(*N*-phenyl-2-naphthylamine)	0.05	38	3.9
1,1′-Bis(*N*-phenyl-2-naphthylamine)	0.05	40	4.1
1,1′-Bis(*N*-phenyl-2-naphthylamine)	0.10	23	4.8[d]
1,1′-Bis(di-2-naphthylamine)	0.05	37	3.8
1,1′-Bis(di-2-naphthylamine)	0.10	19	3.9

[a] Chlorobenzene was used as solvent. [b] Inhibition period. [c] $n = 2ek_1[\mathrm{I}]t/[\mathrm{AH}]$ = number of radicals generated during the inhibition period/number of inhibitor molecules. [d] This run was too weakly inhibited for accurate interpolation of the inhibition period.

The deuterium isotope effect for inhibition by bis-PBN was determined by measuring rates in the presence of H_2O and D_2O (Figure 1).[13] Dividing[14] $R_0(D_2O)$ by $R_0(H_2O)$ yielded a value for $k_5(\mathrm{H})/k_5(\mathrm{D})$ of 3.6. This compares with values of 3.0 to 4.0 for several typical diarylamine antioxidants determined by Brownlie and Ingold[15] (Table II) and establishes hydrogen transfer from the N–H bond (reaction 5) as the rate-determining step of inhibition.

TABLE II

DEUTERIUM ISOTOPE EFFECTS FOR HYDROGEN TRANSFER REACTIONS OF AMINE INHIBITORS

Inhibitor	$k_5(\mathrm{H})/k_5(\mathrm{D})$
Diphenylamine	3.0[a]
N-Phenyl-2-naphthylamine	3.0[a]
N-Phenyl-1-naphthylamine	4.0[a]
1,1′-Bis(*N*-phenyl-2-naphthylamine)	3.6[b]

[a] Styrene at 65°, ref 15. [b] Cumene at 60°.

Kinetic investigations utilizing electron spin resonance[4,12,16] have shown eq 5–8 to be insufficient for description of inhibition by diphenylamine and its derivatives because of the contribution of diaryl nitroxide radicals. *N*-Arylnaphthylamines, however, exhibit negligible nitroxide contribution,[4] and the kinetics[15] and termination products[2] of inhibition by PBN are consistent with eq 1–7. Since inhibition by bis-PBN yields only marginally more nitroxide radicals than PBN,[4] the contribution of nitroxide has been neglected in the kinetics treatment.

The application of eq 9 to the autoxidation of cumene inhibited by bis-PBN is summarized in Figure 2. From the observed value of 5.87 × 10^{-4} for k_3/k_5, a value for k_5 of 1320 M^{-1} sec^{-1} is calculated using Hendry's value[17] of 0.78 M^{-1} sec^{-1} for k_3 at 60°.[18] The value of k_5 is unusually low for an amine antioxidant, as seen by comparison with similar data for various inhibitors in Table III.

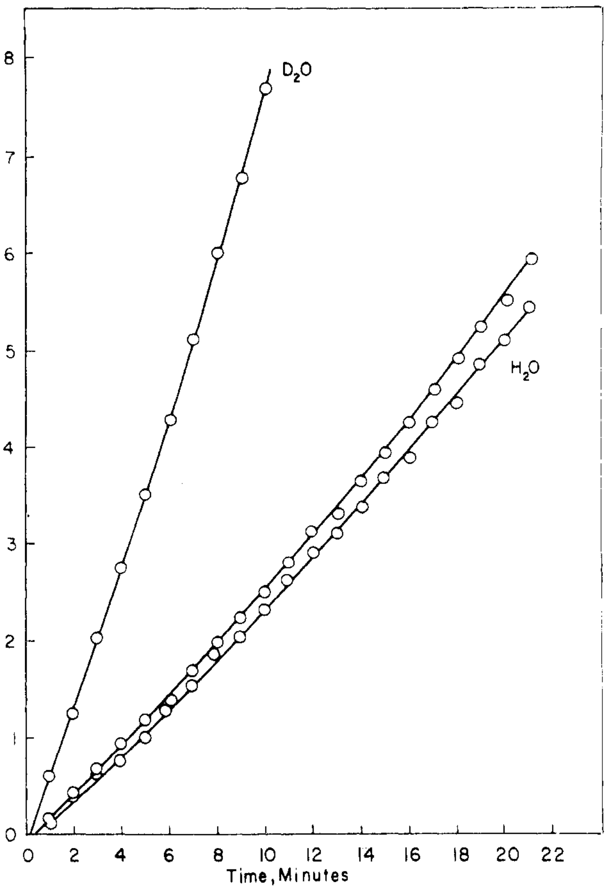
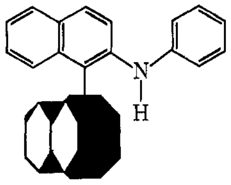
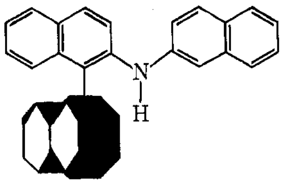


Figure 1.—Inhibition of cumene autoxidation by 1,1′-bis-PBN. Deuterium isotope effect: [AH] = 3.86 × 10^{-4} *M*, [ABN] = 0.05 *M*, [RH] = 3.46 *M* in chlorobenzene at 60°, 100 ml of solution.

Molecular models suggest that the preferred conformations of 1,1′-bis(*N*-phenyl-2-naphthylamine) and 1,1′-bis(di-2-naphthylamine) place the N–H bonds approximately parallel to the opposing naphthyl groups, as illustrated below. (One arylamino group has been omitted from each structure for clarity.) This not only makes the NH bond relatively inaccessible to



k_5 = 1320 M^{-1}sec^{-1}



k_5 = 12,000 M^{-1}sec^{-1}

the attacking peroxy radical but interferes with delocalization of the incipient amino radical into the naphthyl group of bis-PBN during attainment of the transition state. As a consequence of steric hindrance to radical attack and loss of overlap with the naphthyl moiety, bis-PBN is only one-fifteenth as efficient as diphenylamine.

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(13) K. U. Ingold and J. A. Howard, *Nature*, **195**, 280 (1962).

(14) By substituting typical values of concentrations and rate constants in eq 9, it can be shown that this approximation leads to a maximum error of 5% in $k_5(\mathrm{H})/k_5(\mathrm{D})$.

(15) (a) I. T. Brownlie and K. U. Ingold, *Can. J. Chem.*, **44**, 861 (1966); (b) I. T. Brownlie and K. U. Ingold, *ibid.*, **45**, 2419 (1967).

(16) K. Adamic, M. Dunn, and K. U. Ingold, *ibid.*, **47**, 287 (1969).

(17) D. G. Hendry, *J. Amer. Chem. Soc.*, **89**, 5433 (1967).

(18) This value of k_5 is *per molecule;* an approximate value of k_5 *per NH bond* may be obtained by dividing by two.

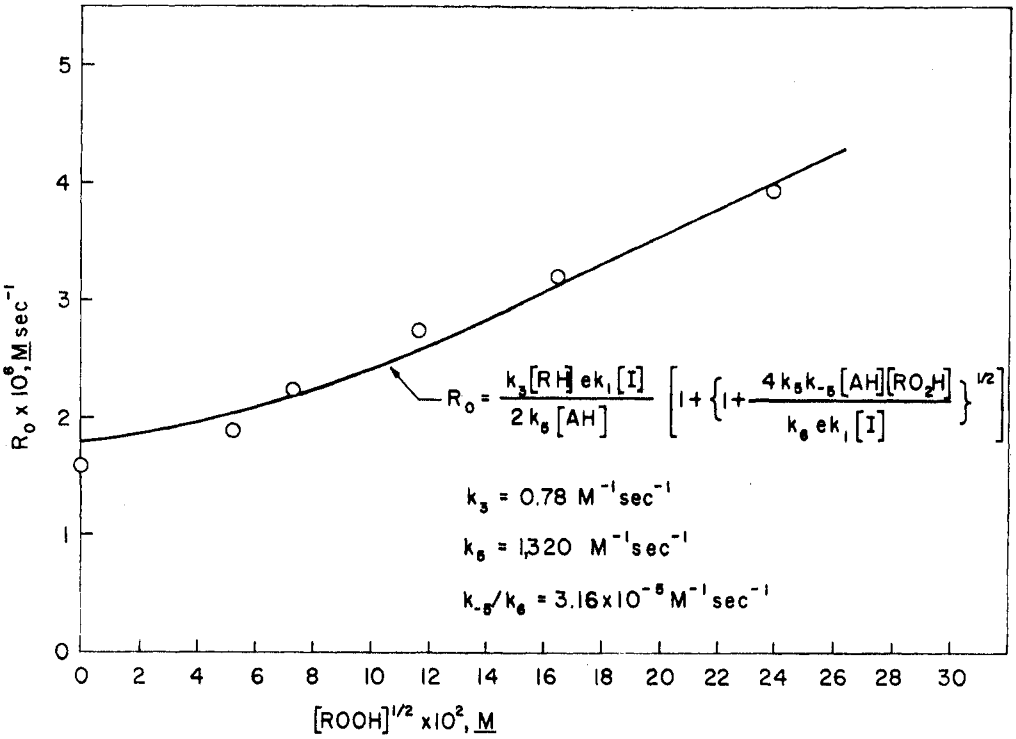

Figure 2.—Inhibition of cumene autoxidation by 1,1′-bis(*N*-phenyl-2-naphthylamine): 0.05 *M* [I], 3.86 × 10^{-4} *M* [AH], 3.46 *M* [RH].

TABLE III

COMPARISON OF RATE CONSTANTS FOR VARIOUS INHIBITORS

Inhibitor	$k_5 \times 10^{-3}$ M^{-1} sec^{-1}	$k_{-5}/k_6 \times 10^7$
Diphenylamine[a]	20	44
N-Phenyl-2-naphthylamine[a]	50	29
N-Phenyl-1-naphthylamine[a]	70	3.6
Di-2-naphthylamine[a]	90	16
2,6-Di-*tert*-butyl-4-methylphenol[a]	17.8	
Phenol[a]	4.9	130
1,1′-Bis(*N*-phenyl-2-naphthylamine)[b]	1.32	316
1,1′-Bis(di-2-naphthylamine)[b]	12	*c*

[a] Styrene, 65°, ref 15. [b] Cumene, 60°, this work. [c] Not determined.

Much more surprising, however, is the extraordinarily high value of k_{-5}/k_6. This implies either a very slow termination (k_6) or a high value of k_{-5}. A distinction cannot be made without more detailed information on the termination processes. In view of the observed hydrogen transfer from tetralin, however, we believe that the reversibility of reaction 5 must be quite high, reflecting enhanced reactivity of the amino radical due to the reduced delocalization described above.

The present results are similar to those of Gardner, Howard, and Ingold, who observed chain transfer of the 2,4,6-tri-*tert*-butylanilino radical with both hydroperoxide and styrene.[3] These observations with hindered amines contrast strongly with the beneficial effects of bulky substituents on phenols for which reactions −5 and 8 can be virtually eliminated.[3,5,7] The anomalous behavior of amines may be due to their degradation chemistry, which is quite complex. Despite several recent studies,[2,4,19] this area is in need of more attention.

Experimental Section

Hydrocarbons, hydroperoxides, and initiator were purified by standard methods. Preparations of the inhibitors have been described.[1]

Initial rates of oxidation were measured in a previously described apparatus,[20] using 100 ml of solution and dropping a glass bucket[15a] containing initiator into the previously thermostated solution. Rates were independent of oxygen pressure and rate of stirring. Oxidation rates have been corrected for nitrogen evolution and oxygen consumption by initiator fragments. The efficiency[21] of 2,2′-azobis(2-methylpropionitrile) at 60° was taken as 0.60 and the specific rate constant of decomposition[22] as 1.15 × 10^{-5} sec^{-1}. Equation 9 was fitted by computer.[23] Representative data are summarized in Table IV.

TABLE IV

KINETIC DATA FOR INHIBITION OF CUMENE AUTOXIDATION BY 1,1′-BIS(*N*-PHENYL-2-NAPHTHYLAMINE) AT 60°

[ROOH] × 10^3 *M*[a]	$R_0 \times 10^6$ *M* sec^{-1} Exptl	Calcd[b]	Difference × 10^6	Difference, %
0.00	1.59	1.81	+0.22	+13.8
2.75	1.89	2.02	+0.13	+6.9
5.45	2.24	2.20	−0.04	−1.8
13.63	2.75	2.62	−0.13	−4.7
27.3	3.22	3.15	−0.07	−2.2
57.8	3.93	4.03	+0.10	+2.5

[a] Other reagents include 0.05 *M* [I], 3.86 × 10^{-4} *M* [AH], 3.46 *M* [RH]; chlorobenzene was used as solvent. [b] Calculated from eq 9 using k_3, 0.78 M^{-1} sec^{-1}; k_5, 1320 M^{-1} sec^{-1}; and k_{-5}/k_6, 3.16 × 10^{-5}.

Registry No.—Bis-PBN, 17704-02-8; 1,1′-bis(di-2-naphthylamine), 4488-22-6; cumene, 98-82-8.

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[20] R. F. Bridger, A. L. Williams, and L. J. McCabe, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 226 (1966).

[21] G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Amer. Chem. Soc.*, **77**, 3244 (1955).

[22] G. A. Russell, *ibid.*, **79**, 3871 (1957).

[23] We are grateful to E. B. Peterson for writing the program for eq 9.