426. *Alkylperoxy-radicals. Part III.* Kinetics of Autoxidations Retarded by Aromatic Amines.*

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The relative reactivities at 60° of various aromatic amines were determined by measuring initial rates of oxidation in a system involving reactions of alkylperoxy-radicals with an amine (AH) or with a standard hydrocarbon (RH = 9 : 10-dihydroanthracene). The initiating radicals were produced by thermal dissociation of 2 : 2 : 3 : 3-tetraphenylbutane and reaction of the resulting radicals with oxygen.

Several types of kinetics were found to occur, depending on the amine investigated and were interpreted on the assumption that amines react in the same way as alkylphenols. Attempts to isolate definite compounds were unsuccessful.

Secondary aromatic amines can be characterized in the same manner as alkylphenols, (1) by the efficiency, *i.e.*, the ratio of the rates of hydrogen abstraction by alkylperoxy-radicals from the amine and from the hydrocarbon respectively, and (2) by the rate of the chain-transfer reaction $A\cdot + RH \longrightarrow AH + R\cdot$. The antioxidant efficiencies of these two classes of compound appeared to be of the same order of magnitude. The presence of large *N*-naphthyl groups completely prevented the occurrence of chain transfer.

Tertiary amines showed no retarding properties but *increased* the rate of oxygen-absorption, indicating the formation from the amine of active radicals capable of adding oxygen.

An insight into the mode of action of alkylphenols as antioxidants was obtained earlier by kinetic investigations of autoxidations retarded by these compounds, as described in Part II.* This work was based on the isolation of the products formed by reaction of the phenols with alkylperoxy-radicals.[1] We have now investigated similarly the mechanism of oxidations retarded by aromatic amines.

The competitive system described in Part II was again employed for the quantitative comparison of the reactivities of the amines. The isolation of products formed by interaction of amines and independently generated alkylperoxy-radicals, however, proved to

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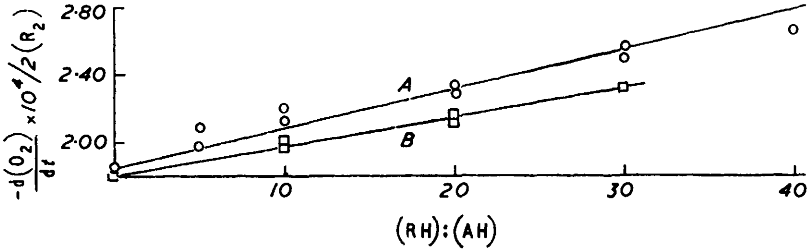
* Part II, *J.*, 1956, 2215.

[1] Part I, *J.*, 1953, 3211.

be extremely difficult. As a result, the interpretation of the kinetic measurements is not as well founded as in the case of the phenolic antioxidants. In many instances, however, the kinetics were comparable to those found for phenols, which makes it possible to draw plausible conclusions about mechanism.

The isolation of products was attempted : (1) by dissociation of 2 : 2 : 3 : 3-tetraphenylbutane in a solution of the amine in the presence of oxygen, and (2) by decomposition of *tert.*-butyl hydroperoxide by cobalt naphthenate in a solution of the amine. Both methods, when applied to *N*-phenyl-β-naphthylamine, yielded a small amount of an oxygen-containing compound that may be a hydroxy-derivative of the amine. In other cases only tars were produced. These negative results stand in contrast to the high yields of products obtained from phenols (Part I) ; the difference may be due to a greater reactivity towards RO•O• of the primary reaction products of RO•O• and amine.

FIG. 1. *A*, *N-Phenyl-β-naphthylamine.* *B*, *N-Phenyl-α-naphthylamine.*



Kinetics.—The kinetics were studied by measuring initial rates of oxygen consumption as a function of intakes of 9 : 10-dihydroanthracene (RH) as standard hydrocarbon, aromatic amine (AH) as retarder, 2 : 2 : 3 : 3-tetraphenylbutane (R_2) as initiator and bromobenzene as inert solvent. The merits of this system as well as the assumptions involved were discussed in Part II. Moreover, the measurement of ***initial rates*** minimizes the kinetic importance of secondary processes which may play a dominant role in the isolation experiments.

From the results it appeared that the amines can be arranged in several groups showing different kinetic behaviours : (*a*) for *N*-phenyl-α- and -β-naphthylamine the initial rate of oxidation is a roughly linear function of the (RH) : (AH) ratio [*] (Fig. 1). (*b*) The initial rates of oxidation retarded by *N*-methylaniline and aniline are linear functions of 1/(AH) (Fig. 2) as well as of (RH) (Fig. 3) ; they may be represented as a linear function of (RH)/(AH) + *c*(RH), where *c* is a constant. (*c*) Oxidations inhibited by *NN'*-di-*sec.*-butyl-*p*-phenylenediamine show a true induction period, the length of which depends on (AH) (Table 2). (*d*) *NN*-Dimethylaniline and triethylamine accelerate oxidation of the standard hydrocarbon. If a system of initiator, *tert.*-amine, and 2 : 6-di-*tert.*-butyl-4-methylphenol as retarder is employed the amine behaves as a chain-carrying hydrocarbon.

The main reactions in the competitive system will be the following : [†]

$$R_2 \xrightarrow{k_D} 2R\cdot \qquad R\cdot + O_2 \longrightarrow RO{\cdot}O\cdot$$

$$RO{\cdot}O\cdot + RH \xrightarrow{k_r} RO{\cdot}OH + R\cdot$$

$$RO{\cdot}O\cdot + AH \xrightarrow{k_b} RO{\cdot}OH + A$$

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[*] Parentheses in such expressions and in the mathematical expressions denote concentrations in moles per 300 ml. (446 g.) of bromobenzene, this being the volume used in all experiments (cf. *J.*, 1956, 2216, footnote) ; $d(O_2)/dt$ is in moles/sec.

[†] In these formulations R• produced in dissociation is $Ph_2MeC\cdot$, but in general the free radical R• is 10-hydro-9-anthryl. This difference does not affect radical-propagation but would be material if products were under consideration.

antioxidant and hydrocarbon competing for the alkylperoxy-radicals. Termination may be effected by interaction of A· radicals, *e.g.*, dimerization,

$$2\mathrm{A}\cdot \xrightarrow{k_d} \mathrm{A}_2$$

The rate of oxidation is then given by eqn. (1) of Part II :

$$-\mathrm{d}(\mathrm{O}_2)/\mathrm{d}t = 2k_{\mathrm{D}}(\mathrm{R}_2)\{1 + k_r(\mathrm{RH})/k_b(\mathrm{AH})\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

With regard to (*a*) above, the retarding action of the *N*-phenylnaphthylamines can therefore be interpreted in terms of this simple mechanism. The type of products formed being unknown, other terminations such as RO·O· + A· ⟶ RO·OA may also be involved; they result in a similar linear dependency of rate on (RH) : (AH) ratio. The antioxidant efficiencies, k_b/k_r, can be evaluated from the slope of the lines in Fig. 1 and are presented in Table 1, where, for comparison, the values of two phenols have been included.

FIG. 2. *Aniline* : *A*, (RH) = 5·0 × 10^{-3}; *B*, (RH) = 2·0 × 10^{-3}. N-*Methylaniline* : *C*, (RH) = 5·0 × 10^{-3}; *D*, (RH) = 2·0 × 10^{-3}.

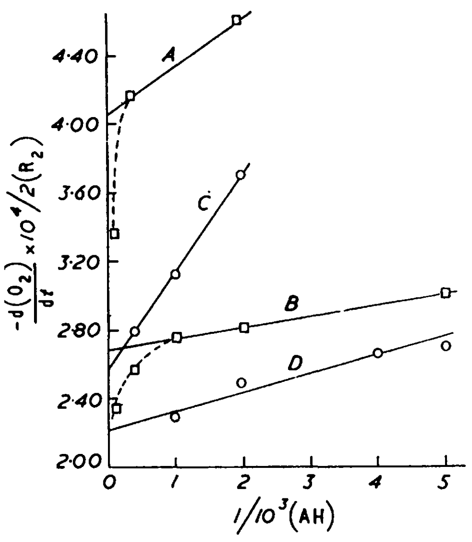
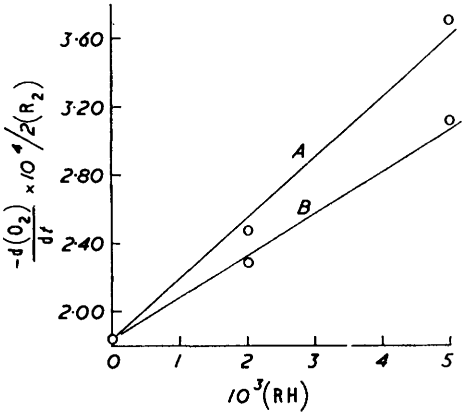


FIG. 3. N-*Methylaniline* : *A*, (AH) = 0·5 × 10^{-3}; *B*, (AH) = 1 × 10^{-3}.



With regard to (*b*) above, *N*-methylaniline probably acts in accordance with the above kinetics including a chain-transfer reaction :

$$\mathrm{A}\cdot + \mathrm{RH} \xrightarrow{k_c} \mathrm{AH} + \mathrm{R}\cdot$$

The rate of oxidation is represented by :

$$-\mathrm{d}(\mathrm{O}_2)/\mathrm{d}t = 2k_{\mathrm{D}}(\mathrm{R}_2)\{1 + k_r(\mathrm{RH})/k_b(\mathrm{AH})\} + k_c\{2k_{\mathrm{D}}(\mathrm{R}_2)/k_dV\}^{\frac{1}{2}}(\mathrm{RH}) \quad . \quad (2)\,*$$

For (RH) = constant, eqn. (2) becomes :

$$-\mathrm{d}(\mathrm{O}_2)\mathrm{d}t = c_1 + c_2(\mathrm{AH})^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The antioxidant efficiency k_b/k_r can be determined from the slopes of plots of eqn. (3)

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* This is the correct form of eqn. (7) of Part II.

(Fig. 2). The values of c_1 can be used to calculate $k_c/k_d^{\frac{1}{2}}$, a measure of the chain transfer. For (AH) = constant, eqn. (2) becomes :

$$-\mathrm{d(O_2)}/\mathrm{d}t = c_3 + c_4\mathrm{(RH)} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

In a plot of $-\mathrm{d(O_2)}/\mathrm{d}t$ against (RH), the intercept is the same for all values of (AH) (Fig. 3).

The results for aniline (Fig. 2) point to the same mechanism, an exception being the behaviour at high concentrations of aniline, the initial rates of oxidation then being lower than correspond to the equation. This suggests the formation by dimerization from aniline of a more efficient antioxidant, for instance an aminodiphenylamine.

TABLE 1.

	Antioxidant efficiency	Chain transfer		Antioxidant efficiency	Chain transfer
α-$C_{10}H_7$·NHPh	104 *	0	NHPhMe	15 *	0·03 †
β-$C_{10}H_7$·NHPh	80 *	0	NH_2Ph	~40 *	~0·07 †
4 : 2 : 1-$C_6H_3MeBu^t$·OH	118	0	*p*-$C_6H_4Bu^t$·OH	80—100	0·0085 †
			p-$C_6H_4(NHBu^s)_2$	>10,000	—

* k_b/k_r. † $k_c/k_d^{\frac{1}{2}}$.

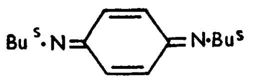
With respect to (*c*) above, *NN'*-di-*sec.*-butyl-*p*-phenylenediamine shows behaviour that has not yet been encountered among alkylphenols. Its action can probably be explained by assuming the operation of the simple mechanism for the phenylnaphthylamines, with the additional condition $k_b \gg k_r$; the oxidation chain involving the hydrocarbon will only be established when nearly all the amine has been consumed. This true inhibition makes it impossible to calculate the antioxidant efficiency in the usual fashion. A lower limiting value can be estimated in the following manner. At a ratio (RH) : (AH) = 400 : 1 the initial rate is less than 4% higher than that for the single initiator. A 4% increase in initial rate would imply an efficiency of 10,000; the actual value may be even higher. The practical value of this extremely efficient antioxidant, however, is limited by its instability towards oxygen.

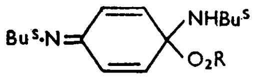
It appears that the amount of inhibitor present is approximately equal to the amount of initiator decomposed in the induction period (Table 2). Hence it follows that *two* alkylperoxy-radicals are inactivated per inhibitor molecule, a fact which points either to dehydrogenation to a quinone imide (I) or to the formation of a peroxide (II) :

TABLE 2. 2 : 2 : 3 : 3-*Tetraphenylbutane* : 1 *mmole*; 9 : 10-*dihydroanthracene* : 20 *mmoles*.

Induction period (min.)	Initiator decomposed (mmole)	Amine (mmole)	Induction period (min.)	Initiator decomposed (mmole)	Amine (mmole)
3·9	0·047	0·050	10·4	0·121	0·150
7·8	0·093	0·100	>20	—	0·250

(I)





(II)

With regard to (*d*) above, tertiary amines are attacked by alkylperoxy-radicals with the production of chain-propagating radicals. This follows from experiments carried out in the absence of 9 : 10-dihydroanthracene, the rate of oxidation being increased by an increase of the amine concentration. We have tried to gain some insight into the oxidation of tertiary amines by employing them as oxidizable substrate and retarding their oxidation by different amounts of a hindered phenol, such as 2 : 6-di-*tert.*-butyl-4-methylphenol. It appeared that the initial rate of oxidation can be represented as a nearly linear function of $(RH)^{\frac{1}{3}}/(AH)^{\frac{1}{3}}$ for triethylamine and of $(RH)^{\frac{1}{2}}/(AH)$ for dimethylaniline. These results cannot be interpreted in terms of a simple mechanism. The oxidation of *NN*-dimethylaniline may follow a pattern similar to that described by Horner *et al.*[2] for its reaction with benzoyl peroxide. Kinetic schemes based on the formation of $PhMeN{\cdot}CH_2{\cdot}$ and $PhMeN{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}$ as chain-carrying radicals lead, however, to relations between the rate of oxidation and (RH) and (AH) that differ essentially from that found experimentally. A complete analysis of the products formed in the oxidation appears to be an essential condition for a better knowledge of the mechanism.

Relations between Structure and Reactivity of Aromatic Amines.—Antioxidant efficiencies of alkylphenols and secondary aromatic amines have the same order of magnitude. It is assumed that their respective reactions with alkylperoxy-radicals follow a similar pattern, the first step probably being the removal of hydrogen from the amino-group. This hydrogen abstraction will be interfered with by the shielding effect of bulky groups bound to the nitrogen. On the other hand, conjugating groups such as β-naphthyl in *N*-phenyl-β-naphthylamine will contribute more to the resonance stabilization of the radical than to that of the amine itself, thus causing a lowering of the N–H bond strength compared with that of amines not having this extra conjugation, for instance, *N*-methylaniline. Attack of alkylperoxy-radicals on the naphthylamine is considerably faster than on *N*-methylaniline. Apparently the conjugative effect of β-naphthyl predominates over its classical steric hindrance.

Both the shielding effect and the lower strength of the N–H bond to be formed will be responsible for the absence of a chain-transfer reaction $A{\cdot} + RH \longrightarrow AH + R{\cdot}$ with the phenylnaphthylamines.

The extremely large antioxidant efficiency of *NN'*-di-*sec.*-butyl-*p*-phenylenediamine can, at least in part, be explained by a weakened N–H bond combined with the large polar effect of the *p*-NHBu^s group.[3, 4]

EXPERIMENTAL (with W. ROEST)

Starting Materials.—*N*-Phenyl-α- and β-naphthylamine, recrystallized from ethanol, had m. p. 61·5—62·0° and 107·5—108·5° respectively.

Triethylamine, aniline, *N*-methylaniline, *NN*-dimethylaniline, and *NN'*-di-*sec.*-butyl-*p*-phenylenediamine were fractionated and had b. p. 88·5—89·0°, 181·5—182·5°, 77·7—78·7°/13 mm., 80·8—81·5°/17 mm., and 173·5—174·5°/17 mm., respectively.

Other starting materials were prepared as described in Parts I and II.

Reactions of N-*Phenyl*-β-*naphthylamine with* tert.-*Butyl Hydroperoxide and Cobalt Naphthenate or with* 2 : 2 : 3 : 3-*Tetraphenylbutane and Oxygen.*—These reactions were performed by procedures similar to those described in Part I. A very small amount of a colourless *substance*, m. p. 167—167·5°, was isolated by percolation of the evaporated reaction mixture over aluminium oxide and recrystallization from toluene–ethanol (Found: C, 82·1; H, 6·1; N, 5·6. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·6; N, 5·9%).

Initial rates of oxidation were determined in the manner given in Part II.

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[2] Horner *et al.*, *Annalen*, 1950, **566**, 69; 1953, **579**, 175, 193.

[3] Russell, *J. Amer. Chem. Soc.*, 1956, **78**, 1047.

[4] Kooyman, van Helden, and Bickel, *Proc. Ned. Akad. Wet.*, 1953, *B*, **56**, 75.