

ANTIOXIDANT ACTIVITY OF N-PHENYL-1,4-PHENYLENEDIAMINE AND ITS DERIVATIVES IN TETRALIN*

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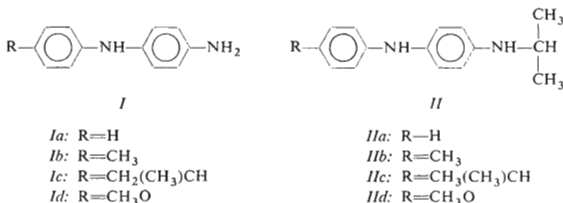
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Using data on the uptake of oxygen in the oxidation of tetralin (60°C, initiated with 2,2'-azobis(isobutyronitrile)), structural effects of N-(4-subst.phenyl)-1,4-phenylenediamines (*I*) and N-(4-subst.phenyl)-N'-isopropyl-1,4-phenylenediamines (*II*) influencing the inhibition of the oxidation were determined. In both types of the antidegradants the antioxidant activity is unfavourably affected by the presence of the methoxy group in position 4 of N-phenyl. N-(4-Alkyl-phenyl) derivatives possess efficiency comparable to, or lower than, that of 4-phenyl derivatives. Compared with *II*, the antioxidant properties of diamines *I* are generally better.

N,N'-Disubstituted derivatives of 1,4-phenylenediamine are the most important technologically applied antidegradants for diene-based rubbers. In rubbers and their vulcanizates they are expected to play a dualistic role, namely, that of antioxidants and antiozonants. All N,N'-disubstituted 1,4-phenylenediamines possess antioxidant properties¹, but only part of them may be used as antiozonants^{2,3}. The former function ensues from the presence of two —NH— groups bound to an aromatic ring, which results in the ability to act as a chain-breaking antioxidant. The structural factors underlying the latter, *i.e.* antiozonant function are still not quite clear, similarly to the mechanism of antiozonant action. An investigation of the effect of structural factors has revealed⁴⁻⁷ that the most effective protection against ozone cracking under static or dynamic conditions is obtained with N,N'-di-sec-alkyl-1,4-phenylenediamines (as sec. alkyls cyclohexyl groups have also been used). However, it was N-sec-alkyl-N'-phenyl-1,4-phenylenediamines which were found to be the most effective flex-cracking antidegradants. These derivatives have yet another technological advantage: they do not have any negative effects on the vulcanization process. The stabilizing efficiency is of course also specifically affected by the character of the vulcanizate and by the conditions of its ageing, which involves thermal, oxidation (effects of oxygen and ozone), photochemical, catalytic (effect of metal ions and active surfaces of fillers), and mechanical processes. The individual processes affect the

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vulcanizate not only in various sequences, but also with various intensity. In order to understand the mechanism of action of the derivatives of 1,4-phenylenediamine one should understand their behaviour under conditions of any of the individual degradation effects. This paper is a continuation of a study of the efficiency and mechanism of antioxidant action of N,N'-di-sec-alkyl-, N-sec-alkyl-N'-aryl- and N,N'-diaryl-1,4-phenylenediamines in the oxidation of various aliphatic hydrocarbons¹. It is concerned with N-aryl-1,4-phenylenediamines (*I*) and N-aryl-N'-isopropyl-1,4-phenylenediamines (*II*) used as antioxidants in the initiated oxidation of tetralin.



EXPERIMENTAL

Antidegradants

* N-Phenyl-1,4-phenylenediamine (*Ia*), m.p. 75°C (isopropyl alcohol). N-(4-Methylphenyl)-1,4-phenylenediamine (*Ib*), prepared according to ref.⁸, hydrogenated in isopropyl alcohol; m.p. 120–2°C. N-(4-Isopropylphenyl)-1,4-phenylenediamine (*Ic*) was prepared similarly to *Ib*, with 4-isopropylaniline used in the synthesis; m.p. 132–4°C. N-(4-Methoxyphenyl)-1,4-phenylenediamine (*Id*) was prepared according to ref.⁹; m.p. 96–7°C. N-Phenyl-N'-isopropyl-1,4-phenylenediamine (*IIa*) was obtained by a repeated crystallization of technical Antioxidant CD (ChZJD Bratislava) from 85% isopropyl alcohol, m.p. 80°C. N-(4-Methylphenyl)-N'-isopropyl-1,4-phenylenediamine (*IIb*) was prepared according to ref.⁸, m.p. 89–89.5°C. N-(4-Isopropylphenyl)-N'-isopropyl-1,4-phenylenediamine (*IIc*) was prepared according to ref.⁸, m.p. 77–9°C. N-(4-Methoxyphenyl)-N'-isopropyl-1,4-phenylenediamine (*IId*) was prepared according to ref.⁹, b.p. 206–10°C/133.3 Pa.

Substrate, Solvent, Initiator

Tetralin was purified according to ref.¹⁰, b.p. 103°C. Chlorobenzene, b.p. 132°C. 2,2'-Azobis(isobutyronitrile) was recrystallized from acetone, m.p. 103°C.

Determination of the Antioxidant Efficiency of 1,4-Phenylenediamines

The antioxidant efficiency was determined by measuring oxygen consumption in the oxidation of a tetralin solution in chlorobenzene (mixed by volume 1 : 1) under atmospheric pressure. Oxidation was carried out in a thermostated volumetric apparatus at 60°C. The initiator concentration was

$5 \cdot 10^{-3}$ mol/l, the concentrations of antidegradants were $5 \cdot 10^{-4}$ and 10^{-3} mol/l. The induction periods, τ (min), were read from the absorption oxygen curves for the individual compounds *I* and *II* using the intersection points of tangents of the curves with the time axis. The induction times τ_5 and τ_{10} were calculated respectively for a consumption of 5 and 10 mmol oxygen/mol tetralin. The relative efficiency, A_r , for the consumption 10 mmol O_2 /mol substrate was calculated as $(\tau_x - \tau_0)/(\tau_s - \tau_0)$, where τ_0 is the induction time of the substrate without antidegradant, τ_s is the induction time of the substrate containing *Ila* (standard), and τ_x is the induction time of the substrate containing the antidegradant under investigation. The slopes of the curves, S (mmol O_2 /min), were calculated for oxygen absorptions after the induction period, using the expression $S/(\tau_{10} - \tau_5)$ (the absorption intercept 5 to 10 mmol O_2 /mol tetralin); the S_r values are summarized in Table I (the ratio between the slopes of the oxygen consumption curves in presence of the antidegradant under investigation and the consumption curves without antidegradant).

RESULTS AND DISCUSSION

Amine antidegradants of the structural type *II* selected for this study are reported as effective antiozonants^{6,7,11-15}. Unlike N-isopropyl-N'-phenyl-1,4-phenylenediamine (*Ila*) or its less toxic analog N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine which at the present time are the antiozonants most in use for vulcanized rubbers, *Iib* through *Iid* contain the alkyl or alkoxy group in position 4 of the phenyl group which represents one of the substituents on the nitrogen atom. According to ref.¹⁶, nonsymmetrically N,N'-disubstituted 1,4-phenylenediamines also possess advantageous physical properties: they are leached from vulcanizates to a smaller extent than symmetrical N,N'-dialkyl- or N,N'-diaryl-1,4-phenylenediamines and are also less volatile than N,N'-dialkyl derivatives.

Compounds *II* were used as antioxidants along with their analogs *I* which contain an aryl substituent on one amino group while the other amino group remains unsubstituted. The results are discussed on the basis of measurements of the oxygen consumption in the oxidation of tetralin containing azobis(isobutyronitrile) as initiator. The results of measurements are summarized in Table I.

The plots of absorption curves of oxygen in the oxidation of tetralin containing *I* and *II* have very distinct induction periods. The absorption of oxygen in presence of *Ic* is an exception which is difficult to explain. At both concentrations of this antioxidant the transition into the stationary stage of oxidation is very slow.

As can be seen from the S_r values, there is no basic difference between the oxidation course of *I* and *II* after the induction period. Hence, it may be inferred that under the experimental conditions used, the effect of the presence of a free amino group— NH_2 (in *I*) on the oxidation course in this stage of the process does not differ from that of the sec-alkyl-NH-group (in *II*). A small but distinct difference in the effect upon oxidation of both types, *I* and *II*, taken for comparison can be observed with antioxidants containing the methoxy group on the phenyl group, i.e. with *Id* and *Iid*. The oxidation is less retarded than in presence of compounds containing the phenyl

group substituted with alkyl groups. Compared with *Ia-c*, or *Ila-c*, *Id* or *Ild* always have lower values of the induction period or induction times τ_5 and τ_{10} . This indicates their generally lower antioxidant activity. In view of the otherwise identical structure, this difference in efficiency may be explained by an unfavourable inductive effect of the methoxyl group on the reactivity of the imino group —NH— in the electrophilic process with radicals RO_2^\cdot . Thus, the first general conclusion drawn from a comparison between *I* and *II* shows that the presence of the alkoxy group in the N-phenyl group does not favour antioxidant action. Compounds N-substituted with the phenyl group or with the 4-alkylphenyl group always had higher antioxidant efficiencies than N-(4-methoxyphenyl) derivatives. In the characterization of the same compounds by static and dynamic antiozonant tests⁶, the methoxy derivative *Ild* was classified as a very effective antiozonant, with no funda-

TABLE I

Oxidation of tetralin in presence of derivatives of 1,4-phenylenediamine. [Initiator] = $5 \cdot 10^{-3}$ mol/l, [tetralin] = 7.338 mol/l of chlorobenzene, 60°C, standard *Ila*. Meaning of abbreviations cf. Experimental

Antioxidant	c mol/l	τ			A_r	S_r
		τ_5	τ_{10}	min		
None	—	—	43	86	—	1.00
<i>Ia</i>	$5 \cdot 10^{-4}$	370	430	490	1.98	0.715
	$1 \cdot 10^{-3}$	420	490	554	0.87	0.672
<i>Ib</i>	$5 \cdot 10^{-4}$	225	336	430	1.68	0.456
	$1 \cdot 10^{-3}$	435	495	555	0.87	0.715
<i>Ic</i>	$5 \cdot 10^{-4}$	286	336	410	1.59	0.577
	$1 \cdot 10^{-3}$	513	565	660	1.06	0.448
<i>Id</i> ^a	$5 \cdot 10^{-4}$	130	246	295	1.02	0.879
<i>Ila</i>	$5 \cdot 10^{-4}$	175	236	290	1.00	0.793
	$1 \cdot 10^{-3}$	473	550	626	1.00	0.560
<i>Ilb</i>	$5 \cdot 10^{-4}$	138	187	240	0.75	0.810
	$1 \cdot 10^{-3}$	345	496	554	0.86	0.741
<i>Ilc</i>	$5 \cdot 10^{-4}$	189	247	308	1.09	0.706
	$1 \cdot 10^{-3}$	280	343	403	0.58	0.715
<i>Ild</i> ^a	$5 \cdot 10^{-4}$	66	115	160	0.36	0.956

^a Insoluble at a concentration of 10^{-3} mol/l.

mental difference from the efficiency of *IIa-c*. This is a consequence of a completely different stabilization mechanism in which ionic processes predominate in contrast with the antioxidation process. In the latter, the chain-breaking antioxidants participate in principle only in radical processes.

It seems interesting to examine the effect of the alkyl group in the N-phenyl group in both *I* and *II*. One can see a negative effect on efficiency compared with *IIa*, especially in the characterization of τ values obtained at a higher concentration of antidegradant. A similar trend can also be seen for *I* in measurements carried out at a lower concentration of antidegradant; at 10^{-3} mol/l, the effect of substitution of the phenyl group is not unambiguous. The data seem to suggest that the presence of the alkyl group does not exert a favourable effect on the antioxidant efficiency. This is surprising, because due to its inductive effect the alkyl group may influence favourably the reactivity of $-\text{NH}-$ in the inhibition process. Moreover, the alkyl group is not bound in a position where its steric influence might impede a reaction with the RO_2^{\cdot} radicals. Measurements performed in tetralin show that the substitution of N-phenyl does not bring any substantial advantages. From the standpoint of antioxidant action, *IIa* should be regarded as a fully satisfactory stabilizer. Its advantages become particularly evident at higher concentration.

The third finding consists in the high antioxidant efficiency of *I* as demonstrated by experimental data. Compounds *Ia-c* are unequivocally commensurate with *IIa* chosen as the standard and regarded by us as an optimally substituted stabilizer from group *II*. At $5 \cdot 10^{-4}$ mol/l, *Ia-c* are even distinctly more effective than *IIa*. When the concentration of antidegradants increases to 10^{-3} mol/l, differences between the relative efficiencies decrease. It may be extrapolated from the data thus obtained that a sufficient antioxidant efficiency of derivatives of 1,4-phenylenediamine may be achieved without substituting both amino groups.

Data are still lacking to draw deeper mechanistic conclusions about the effect of the free amino group in the aromatic 1,4-phenylenediamine system and of the amino radicals derived therefrom on the oxidation process. In no case, however, does the presence of free amino groups impair the antioxidant efficiency compared with *II*, especially if *I* is present at low concentration. If a commercial antidegradant of type *II* contains a compound of type *I* as impurity, these impurities are not harmful with respect to antioxidant action.

Antiozonant tests (30°C , 100 ppm O_3 , 24 or 12 h) carried out with vulcanized rubber Kralex 010-401 and natural rubber SMR-5 (mixtures filled with carbon black, the antidegradant contents 1% and 2%) showed¹⁷ that compounds with free amino groups (*I*) considerably reduce the scorch time of the vulcanizing rubber. This is reflected in a decrease in the optimal cure time. Also, compounds *I* have a lower antiozonant efficiency compared with *II*. The results obviously indicate unfavourable properties of compounds of type *I* in the characterization of the protective action against ozone. In view of the fact that amine antidegradants must play a dual anti-

oxidant and antiozonant role in rubbers as already mentioned, *I* cannot be used in the stabilization of rubbers, in spite of their favourable antioxidant activity verified in a low-molecular weight hydrocarbon.

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