

ANTIOXIDANT ACTION OF 1,4-PHENYLENEDIAMINE ANTIDEGRADANTS IN SELECTED LIQUID HYDROCARBONS*

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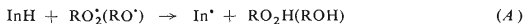
The antioxidant action of six N,N'-disubstituted derivatives of 1,4-phenylenediamine in the oxidation of tetralin, cyclohexene, squalane and squalene initiated with 2,2'-azobis(isobutyronitrile) at 60°C was investigated. The amines under investigation acted as very strong antioxidants. The effect of substitution in positions N,N' on effectiveness is not very essential; it depends on the type of the substrate and does not make possible an unambiguous formulation of the relation between structure and effectiveness. It has been proved unequivocally that retardation of oxidation after completion of the induction period is a result of the formation of derivatives of benzoquinone diimine. The retardative action also is affected by the type of the oxidized hydrocarbon.

Protection of rubbers against oxidation during processing and against weathering, in particular against oxygen and ozone in long-term application, has been investigated for many years. The majority of published papers are however of technical character and deal mainly with physical phenomena accompanying ageing and with an empirical investigation of the stabilization of rubbers, without putting in connection the two different degradation processes and accompanying phenomena^{1,2}. In the protection of rubbers against oxidative degradation and ageing, derivatives of 1,4-phenylenediamine were found to be more advantageous compared with other types of stabilizers³⁻⁶. These data cannot however be used to extrapolate structural relations underlying antioxidant or antiozonant action in this group of antidegradants. In fact, only the primary step of antioxidant action has been elucidated, when the antidegradants behave as chain breakers. The antiozonant mechanism remained obscure, and very little is generally known about transformations of 1,4-phenylenediamines during stabilization and about the properties of compounds thus obtained, although this knowledge is essential for the elucidation of the mechanism through which the antidegradants or products of their transformation remaining in the rubbers after processing may affect the process of atmospheric ageing. The cause leading to a difference between the behaviour of derivatives of 1,4-phenylenediamine as antioxidants and the antiozonant behaviour has not been elucidated either.

N,N'-Disubstituted 1,4-phenylenediamines should be regarded as typical chain-breakers (InH) in the chain oxidation which is the basic process of thermal oxidation of rubbers and their vulcanizates. The process that has been proved to control the

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action of an amine radical scavenger is abstraction of the hydrogen atom in the reaction with radicals RO_2^{\cdot} (ref.⁷). A similar reaction with radicals RO^{\cdot} can also be considered. A very reactive N-centered radical In^{\cdot} is formed as a result,

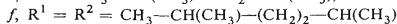
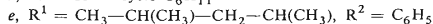
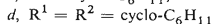
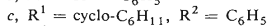
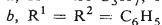
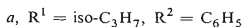
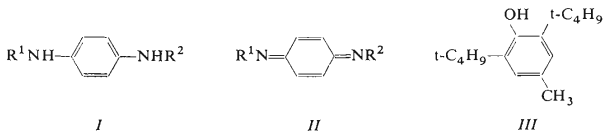


An analysis of the reactivity of amino radicals In^{\cdot} shows that their further participation in the inhibition process involves the C—N and N—N couplings, disproportionation and reactions with the C- and O-centred radicals contained in the oxidized substrate⁸. In vulcanized rubber reactions with various sulphur containing vulcanization agents also cannot be ruled out.

Data reported so far indicate¹ that there is no essential difference between the antioxidant effect of variously N,N'-disubstituted 1,4-phenylenediamines. It has also been reported that a higher effectiveness has been observed with derivatives possessing rather bulky substituents as a result of limitation of the undesired reaction of In^{\cdot} (ref.^{9,10}). These reactions, however, have not been specified in greater detail by identification of their transformation products. A comparison between the action of various N,N'-disubstituted derivatives of 1,4-phenylenediamine in natural rubber has demonstrated¹¹ the strong antioxidant action of N,N'-diarylsubstituted or N-aryl-N'-alkylsubstituted derivatives. On the contrary, N,N'-dialkyl derivatives exhibit only a weak antioxidant action. Due to the complexity of the system used in the investigation, the results cannot be regarded as generally valid.

To elucidate the different action of 1,4-phenylenediamines in the ageing of rubbers, findings obtained with systems simpler than vulcanized rubber are needed, and measurements must be carried out under strictly defined reaction conditions of thermooxidation, photo-oxidation, and ozonolysis. Extrapolation of data obtained under model conditions to conditions of the stabilization of vulcanized rubber must be made with great caution.

This study is concerned with antioxidant action of six variously N,N'-disubstituted 1,4-phenylenediamines (I) in the initiated oxidation of hydrocarbons used as model substrates.



EXPERIMENTAL

Antidegradants

Commercial samples of antioxidants and antiozonants from the group of derivatives of 1,4-phenylenediamine (*I*) were purified by repeated crystallization from methanol, ethanol or isopropyl alcohol in a mixture with water (85 : 15). N-Isopropyl-N'-phenyl-1,4-phenylenediamine (*Ia*, Santoflex IP, Monsanto Chemicals Co., USA), m.p. 79°C; N,N'-diphenyl-1,4-phenylenediamine (*Ib*, Altofane DIP, S. A. Française des Matières Colorantes, France), m.p. 152°C; N-cyclohexyl-N'-phenyl-1,4-phenylenediamine (*Ic*, ASM 4010, Bayer AG, FRG), m.p. 115.5°C; N,N'-dicyclohexyl-1,4-phenylenediamine (*Id*, UOP 26, U.O.P., Chemical Division, USA), m.p. 102 to 104°C; N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine (*Ie*, Vulkanox 4020, Bayer AG, FRG), m.p. 35–37°C; N,N'-bis(1,4-dimethylpentyl)-1,3-phenylenediamine (*If*, Santoflex 77, Monsanto Chemicals Co., USA), $d_{20} = 0.905 \text{ g/cm}^3$.

1,4-Benzoquinonediimines (*II*) derived from *Ia–Id* were prepared by oxidation of the corresponding diamines *I* with silver monoxide¹² or $\text{K}_3\text{Fe}(\text{CN})_6$ in an alkaline medium¹³ and recrystallized from cyclohexane and light petroleum. N-Isopropyl-N'-phenyl-1,4-benzoquinonediimine (*IIa*), m.p. 42–44°C; N,N'-diphenyl-1,4-benzoquinonediimine (*IIb*), m.p. 185°C; N-cyclohexyl-N'-phenyl-1,4-benzoquinonediimine (*IIc*), m.p. 69–70°C; N,N'-dicyclohexyl-1,4-benzoquinonediimine (*IId*), m.p. 175–181°C. Elemental analyses correspond to structures *IIa–IId*.

Hydrocarbon Substrates

Tetralin (VEB Laborchemie Apolda, GDR), b.p. 206.5°C; cyclohexene (J. Dimitrov Chemical Works, ČSSR), b.p. 83°C; 2,6,10,15,19,23-hexamethyltetracosane (squalane, Fluka AG, Switzerland), b.p. 210–215°C/133.3 Pa, purity according to GLC higher than 95%; 2,6,10,15,19,23-hexamethyltetracosane-2,6,10,14,18,22-hexaene (squalene, Eastman Kodak Co., USA), b.p. 284°C/3.33 kPa, purity according to GLC higher than 97%. Tetralin and cyclohexene were purified prior to use by repeated column rectification.

Oxidation of Hydrocarbons

Initiated oxidations of hydrocarbons without and with amine inhibitors were carried out in pure oxygen at 60°C using a six-channelled oxidation apparatus with automatically recorded oxygen consumption¹⁴. The absorption of oxygen was recalculated to millimoles of O_2 per one mole of the substrate. Glass thermostated reactors provided with a manostatically controlled electrolyzers were protected from the access of light. 5 ml chlorobenzene containing $5 \cdot 10^{-3} \text{ mol/l}$ 2,2'-azobis(isobutyronitrile) (Lachema, ČSSR, m.p. 104°C) and 5 ml of hydrocarbon substrate containing antidegradant at concentrations $5 \cdot 10^{-4}$, $1 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ or $1 \cdot 10^{-2} \text{ mol/l}$ were gradually added into the reactor. The first two concentrations of inhibitors corresponded to those of antioxidants, the other two corresponded to the concentrations of antiozonants used in rubbers in practical application. The induction periods, τ (s), were read off from the absorption curves as intersections between the tangents of curves and the time axis; the induction times τ_5 , τ_{10} and τ_{20} (s), were read off from the same curves for consumptions of 5, 10 and 20 mmol O_2/mol of substrate. The slopes of the curves, S (mmol/s), were calculated after completion of the induction period from the ratio $5/(\tau_{10} - \tau_5)$ and $10/(\tau_{20} - \tau_{10})$ for intercepts of absorption of 5–10 and 10–20 mmol O_2/mol substrate, the relative effectiveness values A_r , were calculated for the consumption 10 mmol O_2/mol substrate 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 an

additive used as standard, and τ_x is the induction time of the substrate containing the antidegradant under investigation.

RESULTS AND DISCUSSION

Amine antidegradants for rubbers chosen for this study have properties of antioxidants and/or antiozonants. The effect was investigated of a series of six N,N'-disubstituted 1,4-phenylenediamines of the general structure *I* on the oxidation of model hydrocarbon substrates differing in the content and character of reactive C—H bonds in the molecule. The hydrocarbons used were (*a*) tetralin containing a system of conjugated double bonds and commonly used as a hydrocarbon substrate in the testing of antioxidants, (*b*) cyclohexene possessing an isolated double bond on the saturated unbranched chain, (*c*) 2,6,10,15,19,23-hexamethyltetracosane (squalane) with a branched saturated chain and (*d*) 2,6,10,15,19,23-hexamethyltetracosane-2,6,10,14,18,22-hexaene (squalene) containing a branched unsaturated chain. The latter hydrocarbon is a hexamer of 2-methyl-1,3-butadiene (*i.e.* isoprene) and is therefore a suitable model of natural rubber.

The course of initiated oxidation of a solution of hydrocarbon substrates in chlorobenzene in the absence of antidegradants showed that the oxidation was fastest in the case of squalene ($S = 13\,889 \cdot 10^{-3}$) and proceeded at almost the same rate with cyclohexene ($S = 1\,985 \cdot 10^{-3}$) and tetralin ($S = 1\,984 \cdot 10^{-3}$). The induction period cannot be perceived on the oxidation curves of any of the unsaturated hydrocarbons. Squalane was oxidized very slowly ($S = 0\,31 \cdot 10^{-3}$). The absorption curve of oxygen shows a distinct induction period, $\tau = 9\,720$ s.

An independent investigation demonstrated that chlorobenzene or amine antidegradants alone were not oxidized in the absence of hydrocarbons in chlorobenzene solution in the presence of initiator at 60°C under the conditions of measurement used in the oxidation apparatus.

In order to discuss the oxidation process of hydrocarbons with derivatives of 1,4-phenylenediamine (*I*) and 1,4-benzoquinonediimine (*II*) which have been proved¹⁵ to be the oxidation products of derivatives of *I*, *Ia* and/or the corresponding *IIa* were chosen as standards. The individual additives were compared at equimolar concentrations in various hydrocarbon substrates. The main attention was concentrated on N-isopropyl-N'-phenyl-1,4-phenylenediamine (*Ia*) which at present is the technically most often employed antiozonant for rubbers, and N,N'-diphenyl-1,4-phenylenediamine (*Ib*) which is regarded as one of the most active antioxidants, but does not protect rubbers against ozone ageing. The results are given in Tables I—VII.

The results of oxidation of tetralin inhibited with derivatives of *I* are given in Table I. The shortest induction period is caused by *Id* and *If*, the longest is observed with *Ia*. An increase in the inhibitor concentration from $5 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ mol/l causes the induction period due to most derivatives of *I* to increase 1.6–1.7 times.

A more pronounced increase is due to *Ib* (1.9 times) and *Id* (2.3 times). In order to compare the effectiveness of derivatives of *I* with phenols, the absorption curve was measured of an effective phenolic antioxidant, 2,6-ditert-butyl-4-methyl-phenol (*III*), whose stoichiometric coefficient is theoretically 2, similarly to the derivatives of *I*. On the other hand, however, its relative effectiveness is lower under the conditions used than that of all *I*'s under study, and the process is not retarded after the induction period. Tetralin samples with a high content of derivatives of *I* ($5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ mol/l) did not show completion of the induction period. The absorption of oxygen could be neglected, and within the time interval used (150 h), τ_5 and τ_{10} could not therefore be measured either. This experimental result shows that the derivatives of *I* used at high concentration do not possess any prooxidative effects at 60°. Extrapolation to the conditions of stabilization of rubbers allows us to infer that at a concentration which guarantees an effective protection against ozone, *I* exhibit at the same time a strong antioxidant action without unfavourable side effects.

Differences caused in the induction periods by various derivatives of *I* are relatively

TABLE I

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

Inhibitor	<i>c</i> mol/l	τ	τ_5	τ_{10}	<i>S</i> · 10 ⁴ mmol/s	<i>A_r</i>
		<i>s</i>				
<i>Ia</i>	$5 \cdot 10^{-4}$	18 000	25 200	32 400	8.00	1.00
	$1 \cdot 10^{-3}$	29 400	36 720	45 000	6.00	1.00
<i>Ib</i>	$5 \cdot 10^{-4}$	15 600	24 480	33 120	5.50	1.03
	$1 \cdot 10^{-3}$	30 000	40 320	51 120	4.50	1.15
<i>Ic</i>	$5 \cdot 10^{-4}$	15 000	21 960	29 880	6.50	0.91
	$1 \cdot 10^{-3}$	25 200	31 320	38 520	7.00	0.84
<i>Id</i>	$5 \cdot 10^{-4}$	12 600	36 000	63 000	1.80	2.13
	$1 \cdot 10^{-3}$	28 880	64.800	126 000	0.80	3.04
<i>Ie</i>	$5 \cdot 10^{-4}$	14 400	40 320	69 120	1.70	2.36
	$1 \cdot 10^{-3}$	23 400	46 800	73 800	1.80	1.73
<i>If</i>	$5 \cdot 10^{-4}$	12 600	41 760	79 200	1.30	2.73
	$1 \cdot 10^{-3}$	19 800	47 520	90 000	1.10	2.14
<i>III</i>	$5 \cdot 10^{-4}$	12 600	15 120	18 720	13.90	0.49
Control	—	—	2 880	5 400	19.84	—

small and cannot be used to draw an unambiguous conclusion about the effect of N,N'-disubstitution on the inhibitive effect. The weak influence of substituents' effects on the effectiveness characterized by the induction period confirms the same mechanism of participation of both active—NH— sites of the molecule of *I* according to (A), independently of the substitution of nitrogen atoms (in the range of N,N'-disubstituted *I* investigated by us). Accordingly, the stoichiometric coefficient of all derivatives of *I* is approximately 2 (calculated using ref.¹⁶); each of the—NH— bonds participates in the interruption of one oxidation chain.

During the oxidation process, the derivatives of *I* are gradually transformed and those of *II* are accumulated up to the range of the induction period in which the derivatives of *II* predominate in the oxidized hydrocarbon^{15,17}. Along with *II*, the mixture also contains amino radicals In^* (ref.¹⁸) which participate in the coupling processes⁸. Hence, the experimentally observed inhibitive result in the range of the induction period cannot be attributed only to the derivatives of *I*, but also to their mixture with the transformation products of *I*. Although it is already known that *II* is the main primary product (ref.¹⁵), due to the completely insufficient knowledge

TABLE II

Oxidation of tetralin in the presence of derivatives of 1,4-benzoquinonediimine. [Initiator] = $5 \cdot 10^{-3}$, [tetralin] = 7.338 mol/l of chlorobenzene, temperature 60°C, standard *Ia*

Inhibitor	<i>c</i> mol/l	τ_5	τ_{10}	<i>S</i> · 10 ⁴ mmol/l	<i>A_r</i>
		s			
<i>Ia</i>	$5 \cdot 10^{-4}$	4 680	8 640	12.60	1.00
	$1 \cdot 10^{-3}$	7 920	15 840	6.30	1.00
	$5 \cdot 10^{-3}$	16 920	33 480	3.00	1.00
	$1 \cdot 10^{-2}$	18 720	33 480	3.40	1.00
<i>Ib</i>	$5 \cdot 10^{-4}$	4 860	9 720	10.30	1.33
	$1 \cdot 10^{-3}$	6 300	12 240	8.40	0.65
	$5 \cdot 10^{-3}$	17 100	33 480	3.10	1.00
	$1 \cdot 10^{-2}$	18 000	36 000	2.80	1.09
<i>Ic</i>	$5 \cdot 10^{-4}$	5 400	9 720	11.50	1.33
	$5 \cdot 10^{-3}$	16 200	31 320	3.30	0.92
	$1 \cdot 10^{-2}$	25 200	47 880	2.20	1.51
<i>IId</i>	$5 \cdot 10^{-4}$	26 280	54 000	1.80	15.19
	$1 \cdot 10^{-3}$	28 800	59 400	1.60	5.27
	$1 \cdot 10^{-2}$	34 200	81 000	1.10	2.69

of the properties of this group of reactive compounds their effect on further oxidation of the individual types of hydrocarbons cannot be estimated. From this viewpoint, it is important to examine the absorption process of oxygen after the induction period compared with the oxidation of hydrocarbons not containing an amine anti-degradant. In this stage, one can see a considerable difference in the oxidation rate estimated according to the S values and due to the presence of $Ia-Ic$ compared with the effect of $Id-Ij$. The second group of derivatives of I retards the oxidation of tetralin more strongly. Retardation in the stage after the induction period was explained by an investigation of the oxidation of tetralin in the presence of N,N' -disubstituted 1,4-benzoquinonediimines (II) (Table II). None of them caused the induction period to appear, even at concentrations exceeding $5 \cdot 10^{-3}$ mol/l. On the other hand, however, they retarded oxidation from the very beginning, *i.e.*, acted as retarders. The retardative ability increases with increasing concentration in all II under investigation. IId was the strongest retarder at all concentrations used. Iia and Iib were the weakest retarders. Hence, an analogy exists between the trend of retardative action of the transformation products of derivatives of I observed after the induction period, on the one hand, and the action of pure II . We believe that the different retardative ability of various N,N' -disubstituted II is related to their different chemical stability and reactivity in the oxidized substrate. The difference in long-term stability observed in crystalline II or in their solutions in the nonoxidizing

TABLE III

Oxidation of cyclohexene in the presence of derivatives of 1,4-phenylenediamine. [Initiator] = $5 \cdot 10^{-3}$, [cyclohexene] = 9.858 mol/l of chlorobenzene, temperature 60°C, standard Ia

Inhibitor	c mol/l	τ	τ_5	τ_{10}	$S \cdot 10^4$ mmol/s	A_r
		s				
Ia	$5 \cdot 10^{-4}$	12 600	15 840	19 080	15.40	1.00
	$1 \cdot 10^{-3}$	27 000	31 320	36 000	10.70	1.00
Ib	$5 \cdot 10^{-4}$	11 520	15 480	19 800	11.60	1.05
	$1 \cdot 10^{-3}$	24 120	31 680	37 080	9.30	1.03
Ic	$5 \cdot 10^{-4}$	12 600	18 000	25 200	6.90	1.44
	$1 \cdot 10^{-3}$	25 920	29 520	32 400	17.40	0.88
Id	$5 \cdot 10^{-4}$	9 720	12 960	16 200	15.40	0.79
	$1 \cdot 10^{-3}$	16 200	19 800	24 120	11.60	0.62
Control	—	—	2 520	5 040	19.85	—

medium^{15,17} may become operative also in the medium undergoing oxidation and containing reactive radical and molecular species.

Cyclohexene was oxidized similarly to tetralin. The oxidation of both hydrocarbons was also affected in a similar way by the presence of antioxidants *I* when the process was evaluated using the induction periods (Tables I and III). The inhibition process is concentration-dependent, the order of relative effectiveness of derivatives of *I* in cyclohexene at $c_1 = 5 \cdot 10^{-4}$ mol/l is somewhat different compared with tetralin: $I_d < I_a < I_b < I_c$. The derivatives containing at least one aromatic N-substituent are more effective than the aliphatic N,N'-disubstituted derivative. Another observed difference is a general phenomenon indicating the decrease in the relative effectiveness values due to the decrease of *I* in the oxidized mixture from $5 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ mol/l. A particularly marked decrease in A_r was recorded for *Ic*. At the same time, the result indicates the advantageous antioxidant properties of *Ia* in an olefinically unsaturated hydrocarbon. After completion of the induction period, the retardation of oxidation by the transformation products of amines was less effective than in tetralin. Retardation too was concentration-dependent. Analytically (TLC), complete conversion of *I* into *II* was proved. An independent investigation using derivatives of *II* showed that the latter are the cause of retardation (Table IV). The retardative effect estimated according to the *S* values is weaker than in tetralin (the slopes of absorption curves were 1.9 times larger on the average than with tetralin). Hence, the trend of the effect of transformation products of *I* formed *in situ* during the process of inhibited oxidation is analogous to that of the effect of added *II*.

TABLE IV

Oxidation of cyclohexene in the presence of derivatives of 1,4-benzoquinonediimine. [Initiator] = $5 \cdot 10^{-3}$, [cyclohexene] = 9.858 mol/l chlorobenzene, temperature 60°C, standard *Ila*

Inhibitor	c mol/l	τ_5	τ_{10}	<i>S</i> · 10 ⁴ mmol/s	<i>A_r</i>
		s			
<i>Ila</i>	$5 \cdot 10^{-4}$	3 060	6 120	16.30	1.00
	$1 \cdot 10^{-3}$	3 492	7 020	14.10	1.00
	$5 \cdot 10^{-3}$	4 032	7 560	14.10	1.00
	$1 \cdot 10^{-2}$	4 680	8 640	12.60	1.00
<i>Ilb</i>	$5 \cdot 10^{-4}$	4 680	7 920	15.40	2.67
	$5 \cdot 10^{-3}$	4 680	9 000	11.50	1.57
	$1 \cdot 10^{-2}$	9 000	15 120	8.10	2.80
<i>Ilc</i>	$1 \cdot 10^{-3}$	2 880	6 120	15.40	0.54
	$1 \cdot 10^{-2}$	6 840	10 800	12.60	1.60

It should be pointed out that *Ib* greatly exceeded the relative retardative effectiveness of *Ia* (and thus, the order of substituent's effect was different from that observed in the stabilizing effect of the corresponding derivatives of *I*). It cannot be estimated yet to what extent this phenomenon is related to the observed stronger reactivity of *Ia* in the inert medium¹⁷ or in the reaction with ozonides¹⁹.

The oxidation of squalane alone was slow compared with the preceding hydrocarbons. The saturated hydrocarbon substrate not containing an activating olefinic double bond was very effectively stabilized against the initiated oxidation by using the derivatives of *I* already at the lowest concentration, $5 \cdot 10^{-4}$ mol/l (Table V). All the derivatives of *I* possessed protective effects expressed through the extension of the induction period and a weak retardative effect after the induction period which was checked by a model application of *Ib*.

The oxidation of a solution of polyisoprene and effects from the part of the additives are best modelled by the low-molecular analog of polyisoprene – squalene. It is oxidized more quickly than the preceding hydrocarbons, and the absorption of oxygen is very markedly affected by derivatives of *I* (Table VI). The effects of N,N' substitution are little pronounced. The relative effectiveness of most of *I* under investigation is very close to *Ia*. Similarly to the other hydrocarbons, with the antioxidant concentration increasing to $1 \cdot 10^{-3}$ mol/l in the homogeneous medium of oxidation performed in solution the advantageous properties of *Ia* become apparent; *Ia* appears to be the relatively strongest antioxidant. In the presence of all derivatives of *I*, the oxidation is distinctly retarded after completion of the induction period. This again is a consequence of formation of *II*. Their retardative ability in stages following the induction period is marked in squalene and is concentration-

TABLE V

Oxidation of squalane in the presence of derivatives of 1,4-phenylenediamine and benzoquinone-diimine. [Initiator] = $5 \cdot 10^{-3}$, [squalane] = 1.910 mol/l of chlorobenzene, temperature 60°C, standard *Ia*

Inhibitor	<i>c</i> mol/l	τ	τ_5	τ_{10}	<i>S</i> · 10 ⁴ mmol/s	<i>A_r</i>
		s				
<i>Ia</i>	$5 \cdot 10^{-4}$	30 600	50 400	81 000	1.60	1.00
<i>Ib</i>	$5 \cdot 10^{-4}$	46 800	66 600	90 000	2.10	1.25
<i>Ic</i>	$5 \cdot 10^{-4}$	36 000	56 520	86 400	1.70	1.15
<i>Ib</i>	$5 \cdot 10^{-4}$	9 720	30 600	50 400	2.50	0.15
Control	—	9 720	28 800	45 000	3.10	—

-dependent. According to the results (Table VII), the most pronounced effect at all concentrations applied was achieved with *Ila*.

It should be pointed out, however, that the effect of quinonediiimines on the oxidation of squalene is quantitatively different from that on all preceding hydrocarbons containing a saturated chain or one olefinic or diene bond. The presence of any of *II* under investigation in squalene causes a distinct induction period (Table VII). This result is indicated by a weak antioxidative action of *II* and is in agreement with data given for rubber¹³. This is probably due to the presence of a major number of isolated double bonds C=C in one hydrocarbon molecule, and hence also of different interactions in the oxidized system hydrocarbon-additive. Compound *Ile* in vulcanized rubber was found to possess antioxidant activity comparable with the corresponding N,N'-disubstituted *I*. At the same time, the authors observed the formation of *I* from *II* during ageing. A similar effect was detected¹⁵ in the ageing of solid *II* or their solution in inert solvents. On the other hand, however, no formation of *I* was detected in the oxidation of hydrocarbons in the presence of *II*. The

TABLE VI

Oxidation of squalene in the presence of derivatives of 1,4-phenylenediamine. [Initiator] = $5 \cdot 10^{-3}$, [squalene] = 2.090 mol/l of chlorobenzene, temperature 60°C, standard *Ia*

Inhibitor	<i>c</i> mol/l	τ			<i>S</i> · 10 ⁴ mmol/s	<i>A_r</i>
		s				
<i>Ia</i>	$5 \cdot 10^{-4}$	18 800	21 600	27 720	16.30	1.00
	$1 \cdot 10^{-3}$	37 800	46 800	55 080	12.10	1.00
<i>Ib</i>	$5 \cdot 10^{-4}$	18 000	22 680	28 800	16.30	1.05
	$1 \cdot 10^{-3}$	38 520	45 720	54 000	12.10	0.98
<i>Ic</i>	$5 \cdot 10^{-4}$	16 200	21 600	26 280	21.40	1.00
	$1 \cdot 10^{-3}$	37 800	45 000	52 200	13.90	0.96
<i>Id</i>	$5 \cdot 10^{-4}$	14 400	18 720	23 400	21.40	0.86
	$1 \cdot 10^{-3}$	28 800	37 800	46 800	11.10	0.80
<i>Ie</i>	$5 \cdot 10^{-4}$	21 600	26 280	32 400	16.30	1.23
	$1 \cdot 10^{-3}$	34 200	38 880	45 720	14.60	0.83
<i>If</i>	$5 \cdot 10^{-4}$	18 000	23 400	30 600	13.90	1.09
	$1 \cdot 10^{-3}$	27 000	34 200	45 000	9.30	0.72
Control	—	—	1 080	1 800	138.90	—

different results obtained indicate that the mechanism of action of such different systems as *II* should always be evaluated only for a certain defined substrate and reaction conditions. Generalization cannot be made until after several model hydrocarbon substrates have been compared with the polymer. It cannot be ruled out that in rubbers the favourable effect of *II* on long-term ageing also involves the ability of *II* to act as a vulcanizing agent in the simultaneous deactivation of the C-centered radicals formed in the process.

All these findings indicate the necessity of a cautious interpretation of data on the effectiveness of derivatives of 1,4-phenylenediamine in various low-molecular hydrocarbons used as substrates in the estimation of the antioxidant action of amine anti-degradants in rubbers. However, due to the complexity of the polymeric system and to the role played by various physical relations given by its microheterogeneity, by the limited compatibility of the components or by the diffusion and migration phenomena²⁰, some basic parameters of the mechanism of action must be determined separately in the homogeneous solution of low-molecular weight hydrocarbons. It is obvious that a more exact extrapolation of data is allowed using a model substrate with a higher structural similarity to rubber.

A comparative study of a whole series of derivatives of *I* in four different hydrocarbons showed that there are only very small differences between the effects of N,N-disubstitution on the antioxidant activity measured under comparable conditions

TABLE VII

Oxidation of squalene in the presence of derivatives of 1,4-benzoquinonediimine. [Initiator] = $5 \cdot 10^{-3}$, [squalene] = 2.090 mol/l of chlorobenzene, temperature 60°C, standard *IIa*

Inhibitor	<i>c</i> mol/l	τ			<i>S</i> · 10 ⁴ mmol/s	<i>A_r</i>
		τ	τ_{10}	τ_{20}		
<i>IIa</i>	$5 \cdot 10^{-4}$	1 080	7 200	14 040	14.60	1.00
	$5 \cdot 10^{-3}$	1 440	7 200	14 040	14.60	1.00
	$1 \cdot 10^{-2}$	1 800	9 360	18 000	11.60	1.00
<i>IIb</i>	$5 \cdot 10^{-4}$	1 800	5 760	10 080	23.10	0.76
	$5 \cdot 10^{-3}$	1 800	6 840	12 240	18.50	0.94
	$1 \cdot 10^{-2}$	2 880	7 560	13 680	16.30	0.78
<i>IIc</i>	$5 \cdot 10^{-4}$	720	4 320	9 000	21.40	0.53
	$5 \cdot 10^{-3}$	1 800	6 480	13 320	14.60	0.88
<i>IId</i>	$1 \cdot 10^{-3}$	1 080	9 000	16 200	13.90	—

A comparison between the effectiveness of *Ia* and *Ib*, *i.e.* of amines especially important from the viewpoint of practical protection of rubbers revealed that in tetralin, cyclohexene and squalane *Ib* is a 1.1–1.2 time more effective antioxidant than *Ia*. In squalene, *i.e.* in a model which resembles rubber most by its structure, the antioxidant activity of both antidegradants is the same.

We do not want to derive from data provided by our measurements any structural dependence which is operative in the effectiveness of variously *N,N'*-disubstituted derivatives of 1,4-phenylenediamine. Differences in the order of effectiveness determined in various hydrocarbons are only small. If such unessential differences in the effectiveness of *I* reported in the literature were attributed to substituent's effects^{9,10,21}, the conclusions cannot be generalized or regarded as a sufficient proof of the existence of a relation between the structure and antioxidant action, because these data differ also when reported by different authors.

Completely novel is the experimental proof of the mechanism of action of various *N,N'*-disubstituted *I* involving the participation of *II* as main transformation products of *I* in the process of inhibited oxidation. The reaction mixtures formed in the course of oxidation of all hydrocarbons under investigation containing amine antidegradants were analyzed by the TLC and LC methods. It was found¹⁷ that the transformation products of *I* in all cases contain 1,4-benzoquinonediimines *II*. These are gradually accumulated and become predominant in the range of the induction period. At concentrations of *I* exceeding $5 \cdot 10^{-3}$ mol/l, the mixture after completion of the oxidation still contains, under experimental conditions (150 h), a large part of the unreacted original amine. An independent investigation revealed that the forming *II* are the cause of retardative effect in all types of the model hydrocarbons under study. The retardation mechanism due to *II* and estimated according to the process of oxygen absorption differs from the chain-breaking action of the derivatives of *I*. The concentration dependence suggests a radical scavenging process through a conjugated system of double bonds of *II*, which is less effective than the action of *I*. In the retardation of oxidation of hydrocarbons with one or two double bonds there was no induction period at all. On the other hand, in squalene the presence of *II* gave rise to an induction period before the retardation stage. This inhibitive quality of *II* can be assigned to the presence of a system of unsaturated bonds in the hydrocarbon and can therefore be extrapolated also for the action in rubber.

We demonstrated at the same time¹⁷ that reaction mixtures after oxidation inhibited with *II* contained only the original *II*. Hence, under the working conditions used and within the time interval under investigation, no further transformations of these primary oxidation products of 1,4-phenylenediamines take place. On the contrary, under the more complicated conditions of natural ageing, where the stabilized hydrocarbon substrates are exposed to solar radiation and to the accidental catalytic action of impurities, further transformations of *II* were proved to occur in the system^{22,23}.

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