

THE EFFECT OF 1,4-PHENYLENEDIAMINE ANTIDEGRADANTS ON THE PHOTO-OXIDATION OF SELECTED LIQUID HYDROCARBONS*

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Received May 2nd, 1983

Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

The effect of six N,N'-disubstituted 1,4-phenylenediamines (*I*) and four derivatives of 1,4-benzoquinonediimine (*II*) on the photo-oxidation of tetralin, squalane and squalene at 35°C and radiation 300–400 nm was investigated by oxygen uptake measurements. Due to irradiation, the anti-oxidant effectiveness of *I* is so restricted that the induction period did not appear in any of the photo-oxidized hydrocarbons. On the other hand, however, owing to the presence of *I*, there is a strong retardation of the photo-oxidation of hydrocarbons connected with the transformation of *I* in the oxidized hydrocarbon to *II*. Benzoquinonediimines are able to scavenge radicals involved in the propagation step and provide a screening effect. The retardant efficiency of *II* was proved by model investigation. Hence, *II* play a pronounced role in the mechanism of photo-oxidation of hydrocarbons stabilized with *I*.

N,N'-Disubstituted 1,4-phenylenediamines are very effective antioxidants in both low-molecular weight and polymeric hydrocarbons. Some of them act as antiozonants in elastomers based on dienes. The mechanism of their action in thermal processes has been discussed recently¹.

With respect to the atmospheric ageing of polymers, it is important to know the effect of secondary aromatic monoamines and 1,4-phenylenediamines in the photo-oxidation. Only very few data on this process are available. Studies of Dunn^{2,3} performed at 25°C in peroxide vulcanizate of natural rubber stabilized with N-phenyl-2-naphthylamine and N-phenyl-1-naphthylamine and with a series of N,N'-disubstituted 1,4-phenylenediamines proved that the former type of aromatic amines sensitized the initial phase of photo-oxidation at 313 and 365 nm. At comparable conditions, various N,N'-disubstituted 1,4-phenylenediamines inhibited the photo-oxidation at 313 nm from the beginning of the reaction². At 365 nm, a slight increase in the initial degradation rate was observed in the presence of all tested phenylenediamines³. Subsequently, the photo-oxidation was inhibited, presumably by coloured transformation products of phenylenediamines. The most serious initial degradation was observed with N,N'-dimethyl-N,N'-bis(1-methylpropyl)-1,4-phenylenediamine.

Results of some scarce papers indicate reactions of 1,4-phenylenediamines during the photo-

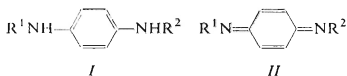
* Part XCIV in the series Antioxidants and Stabilizers: Part XCIII: Polym. Bull. 9, 121 (1983).

-oxidation, N,N,N',N'-tetramethyl-1,4-phenylenediamine is photo-oxidized with RO[•] radicals (methoxyl⁴, ethoxyl and isopropoxyl⁵) to the cation-radical; the alkoxy radical formed transiently from diphenylmethanol or 1-phenylethanol reacts with N,N,N',N'-tetraphenyl-1,4-phenylenediamine in a similar way⁶. The formation of more complicated reaction products *via* N-N and N-C couplings may be expected in the photo-oxidation of N-unsubstituted 1,4-phenylenediamine. This ensues from the formation of an oligomeric polyamine described in ref.⁷. Direct oxidation with oxygen to a nitrogen-centered radical and its further oxidation and coupling reactions are considered as taking place in the process.

The photo-oxidation mechanism of N,N'-diphenyl-1,4-phenylenediamine was investigated in an acid medium by means of flash photolysis⁸. The reaction product is the corresponding 1,4-benzoquinonediimine. The process is a reversible one, and semiquinone is transiently formed both in the photo-oxidation of diamine and in the photoreduction of quinonediimine. The same radical intermediate was also proved to be generated in the thermal oxidation⁹. The quantum yield of photo-oxidation of N,N'-diphenyl-N,N'-dimethyl and N,N'-diphenyl-1,4-phenylenediamine in chloroform at 366 nm is higher than unity. The authors assume that both a thermal and a photochemical process participate in the reaction¹⁰. There was no oxygen absorption in the irradiation of N,N'-diphenyl, N,N'-dimethyl-N,N'-diphenyl and N,N,N',N'-tetraphenyl-1,4-phenylenediamine in nonhalogenated solvents (ethanol, benzene); only the fluorescence of 1,4-phenylenediamines could be detected¹⁰. In the photo-oxidation of 1,4-phenylenediamines the transiently formed radical intermediate may take part in the subsequent reactions. For instance, irradiation of the cation-radical of N,N,N',N'-tetraphenyl-1,4-phenylenediamine at 366 nm in benzyl alcohol evokes the reduction of the former to N,N,N',N'-tetraphenyl-1,4-phenylenediamine, and the photo-oxidation of benzyl alcohol to the corresponding aldehyde⁶. The photocatalytic action of the cation-radical of N,N,N',N'-tetraphenyl-1,4-phenylenediamine in diphenylmethanol or 1-phenylethanol gives rise to the corresponding symmetrical ethers; at the same time, the cation-radical is recycled *via* two successive electron transfers⁶.

In the presence of a suitable sensitizer, molecular singlet oxygen ¹O₂ may also be involved in the photo-oxidation process of 1,4-phenylenediamines. Its participation in the photo-oxidation of rubber stabilized with aromatic amines is considered in ref.¹¹ According to ref.¹², the rate of oxidation of a benzene solution of natural rubber with singlet oxygen is reduced with N-cyclohexyl-N'-phenyl-1,4-phenylenediamine. This probably ensues from the ability of some aromatic amines, and among them, N-isopropyl-N'-phenyl, N-cyclohexyl-N'-phenyl and N,N,N',N'-tetramethyl-1,4-phenylenediamine, to quench effectively ¹O₂ in solution^{12,13}. The effectiveness of quenching varies in the series tertiary > secondary > primary amine¹³. The rate constant of quenching of ¹O₂ ref.^{12,14} at 0° and 25°C is of the order of magnitude 10⁸–10⁹ M⁻¹ s⁻¹. According to ref.¹⁵, a typical product of the reaction between ¹O₂ and N,N,N',N'-4,5-hexamethyl-1,2-phenylenediamine was isolated in the presence of Bengal red. The reaction between derivatives of 1,4-phenylenediamine and singlet oxygen may also be affected by the medium: thus, *e.g.*, N,N,N',N'-tetramethyl-1,4-phenylenediamine is oxidized in H₂O and D₂O with singlet oxygen in a process sensitized with erythrosine at 530 nm to Wurster blue¹⁶, but the same derivative in 1,3-diphenylfuran¹³ or methanol¹⁵ does not react with ¹O₂ in a system sensitized with Bengal red. The structure of the starting diamine also plays a part in the sensitized photo-oxidation: it has been reported¹⁵ that N,N,N',N'-tetramethyl-1,4-phenylenediamine does not absorb oxygen, unlike a similarly tetrasubstituted derivative of 1,2-phenylenediamine. This result seems very surprising, as there is no formal reason for such a difference in behaviour. Data on the photo-oxidation of N,N,N',N'-tetrasubstituted phenylenediamines which do not contain any hydrogen atom bound on nitrogen and are thus involved in a completely different stabilizing mechanism than secondary aromatic amines, mainly operative as stabilizers, are of a rather minor importance for the stabilization process.

In order to obtain the necessary basic data on the effect of 1,4-phenylenediamines on the photo-oxidation of hydrocarbons, we selected six technically important N,N'-disubstituted phenylenediamines *Ia–Ij*. Their stabilization activity is important for unsaturated or saturated carbon chain hydrocarbon polymers. The oxidation was studied using liquid hydrocarbons: tetralin, 2,6,10,15,19,23-hexamethyltetracosane (squalane) and 2,6,10,15,19,23-hexamethyltetracosane-2,6,10,14,18,22-hexaene (squalene).



- I, II:* a, $\text{R}^1 = \text{iso-C}_3\text{H}_7$, $\text{R}^2 = \text{C}_6\text{H}_5$
 b, $\text{R}^1 = \text{R}^2 = \text{C}_6\text{H}_5$
 c, $\text{R}^1 = \text{cyclo-C}_6\text{H}_{11}$, $\text{R}^2 = \text{C}_6\text{H}_5$
 d, $\text{R}^1 = \text{R}^2 = \text{cyclo-C}_6\text{H}_{11}$
 e, $\text{R}^1 = \text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)$, $\text{R}^2 = \text{C}_6\text{H}_5$
 f, $\text{R}^1 = \text{R}^2 = \text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)$

EXPERIMENTAL

Antidegradants

Commercial samples of antioxidants and antiozonants from the group of derivatives of 1,4-phenylenediamine (*I*) were purified by repeated crystallization from a mixture of methanol, ethanol or isopropyl alcohol with water (85 : 15). N-Isopropyl-N'-phenyl-1,4-phenylenediamine (*Ia*, Santoflex IP, Monsanto Chemicals Co., USA), m.p. 79°C, λ_{max} 290 nm; N,N'-diphenyl-1,4-phenylenediamine (*Ib*, Altofane DIP, S. A. Française des Matières Colorantes, France), m.p. 152°C, λ_{max} 304 nm; N-cyclohexyl-N'-phenyl-1,4-phenylenediamine (*Ic*, ASM 4010, Bayer AG, FRG), m.p. 115.5°C, λ_{max} 290 nm; N,N'-dicyclohexyl-1,4-phenylenediamine (*Id*, UOP 26, U.O.P., Chemical Division, USA), m.p. 102–104°C, λ_{max} 257, 318 nm, N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine (*Ie*, Vulkanox 4020, Bayer AG, FRG), m.p. 35–37°C, λ_{max} 290, 430 nm; N,N'-bis-(1,4-dimethylpentyl)-1,4-phenylenediamine (*If*, Santoflex 77, Monsanto Chemicals Co., USA), d_{20} 0.905 g/cm³, λ_{max} 250, 322, 420 nm.

1,4-Benzoquinonediimines (*II*) were prepared by the oxidation of diamines *Ia–Id* with silver monoxide or with $\text{K}_3\text{Fe}(\text{CN})_6$ in an alkaline medium and recrystallized from cyclohexane and light petroleum. N-Isopropyl-N'-phenyl-1,4-benzoquinonediimine (*Iia*), m.p. 42–44°C, λ_{max} 292, 421 nm; N,N'-diphenyl-1,4-benzoquinonediimine (*Iib*), m.p. 185°C, λ_{max} 304, 442 nm; N-cyclohexyl-N'-phenyl-1,4-benzoquinonediimine (*Iic*), m.p. 69–70°C, λ_{max} 300, 420 nm; N,N'-dicyclohexyl-1,4-benzoquinonediimine (*Iid*), m.p. 175–181°C, λ_{max} 290, 475 nm. Elemental analyses are in agreement with the respective structures *Iia–Iid*.

Hydrocarbon Substrates

Tetralin (Laborchemie Apolda, GDR), b.p. 206.5°C, purified by rectification; 2,6,10,15,19,23-hexamethyltetracosane (squalane, Fluka AG, Switzerland), b.p. 210–215°C/133.3 Pa, GLC purity 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/3.3 kPa, GLC purity higher than 97%.

Photo-oxidation

Hydrocarbons, either pure or containing an amine stabilizer at concentrations (c) $5 \cdot 10^{-4}$, $1 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ or $1 \cdot 10^{-2} \text{ mol l}^{-1}$ were oxidized in pure oxygen at 0.1 MPa and 35°C in a quartz cylindrical cell (optical path 15 mm) provided with a magnetic stirrer. Samples (8 ml) were irradiated in an apparatus manufactured by Schoeffel Instrument Corp. (USA), type 0102, with a xenon lamp OSRAM XBO 900 W, the infrared part of the spectrum has been removed by means of a liquid filter and the wavelength was restricted to 300–400 nm using a glass filter UG 2 (1 mm, Jena Glaswerk Schott & Gen., GDR). The constant initial light intensity (2.2 mW/cm^2) was measured with an adapted photodiode (Tesla 1 PP 75) calibrated with an LPC R_c-3960 (Laser Precision Corp., USA) radiometer, and actinometrically with ferrioxalate. The change in the light intensity was recorded continuously. The rate of photo-oxidation was measured using an apparatus with automatically recorded oxygen uptake. The absorption times $\tau_{0.5}$, $\tau_{1.0}$ and $\tau_{1.5}$ (s) were determined graphically from the absorption curves as intersections of tangents of the curves with the time axis for the oxygen uptake of 0.5, 1.0 and 1.5 mmole of oxygen per mole of substrate. The slope of the curves S (mole of oxygen per mole of substrate per second) was calculated for two intercepts of absorptions as follows $S_1 = 0.5/(\tau_{1.0} - \tau_{0.5})$ and $S_2 = 0.5/(\tau_{1.5} - \tau_{1.0})$. The relative slopes of curves S_r were calculated from the ratios $S_{r1} = S_{x1}/S_{s1}$ and $S_{r2} = S_{x2}/S_{s2}$, where the slopes of curves S_x correspond to the antidegradant used as a standard, and the index S_x holds for the studied antidegradant in the same concentrations. The relative activities A_{r1} (for $\tau_{0.5}$) and A_{r2} (for $\tau_{1.0}$) were calculated from the relation $(\tau_x - \tau_0)/(\tau_x - \tau_0)$, where τ_0 is the induction time for the substrate without antidegradant, τ_x is the induction time for the substrate containing antidegradant as the standard, and τ_x is the induction time of the substrate containing the studied antidegradant in the same concentration as the standard.

RESULTS AND DISCUSSION

The effect of aromatic amine antioxidants on the photo-oxidation of hydrocarbons was investigated using six technically important derivatives of 1,4-phenylenediamine *1a–1f*. These compounds are used in the stabilization of elastomers based on dienes against oxidation with oxygen or ozone. The antidegradation activity of phenylenediamines in the photo-oxidation which is an important part of atmospheric ageing remains however unknown. In carbon black loaded elastomers deterioration due to photoprocesses need not be taken into account due to the efficient light screening effect of carbon black, while in unloaded elastomers or polyolefins photo-oxidation must be borne in mind.

We report results obtained using some selected liquid hydrocarbons. Tetralin, 2,6,10,15,19,23-hexamethyltetracosane (squalane) and 2,6,10,15,19,23-hexamethyl-tetracosane-2,6,10,14,18,22-hexaene (squalene, hexamer of isoprene) which may be regarded as a low-molecular weight model of natural rubber were oxidized at 35°C under irradiation in the range of wavelength 300–400 nm. In the absence of antidegradants, squalene which contains a branched carbon chain with a system of isolated double bonds was oxidized fastest under the conditions used ($S = 16.5 \cdot 10^{-8} \text{ s}^{-1}$). Tetralin ($S = 4.5 \cdot 10^{-8} \text{ s}^{-1}$) and squalane ($S = 2.7 \cdot 10^{-8} \text{ s}^{-1}$) were oxidized more slowly. The order of oxidizability of hydrocarbons is the same as

in the thermal oxidation initiated with 2,2'-azobis(isobutyronitrile), but the rate of photo-oxidation is lower by 1–2 orders of magnitude.

N-Isopropyl-N'-phenyl-1,4-phenylenediamine (*Ia*) was used as the standard in comparing the effect of the particular N,N'-disubstituted 1,4-phenylenediamines: it is the technically most important amine antidegradant for elastomers.

An analytical investigation by means of the LC and TLC methods has revealed that similarly to thermal oxidation, in the oxidation of both saturated and unsaturated hydrocarbons stabilized with N,N'-disubstituted 1,4-phenylenediamines *Ia–Ij*, the corresponding N,N'-disubstituted 1,4-benzoquinonediimines are formed first. Other primary transformation products of 1,4-phenylenediamine were not observed under the experimental conditions used. The chromatograms were more complicated, however, because products of the photo-oxidation of hydrocarbons were represented in a much higher number and quantity than in the thermo-oxidation. Formation of 1,4-benzoquinonediimines *II* may involve the oxidation with ROO[•] radicals or with oxygen. The former possibility was proved unequivocally¹⁹. Another important difference consisted in a fast photo-oxidation of *I* to *II* compared with thermal oxidation. *II* appeared in the reaction mixture already from the beginning of the photo-oxidation¹⁸. The fast photo-oxidation of *Ia, Ib, Ic* with ROO[•] radicals ensues also from a comparative study carried out by Goda²⁰ in the thermal and photochemical oxidation initiated with 2,2'-azobis(isobutyronitrile) at 50°C. The ratio of the rate constants of the reaction of tetralyl hydroperoxyl with tetralin and diamines *Ia–Ic* was always lower in the photoprocess. This explains the fast depletion of *I* in the oxidized hydrocarbon and accumulation of primary molecular products (*i.e.*, *II*), while indicating at the same time the possible participation of radical intermediates formed

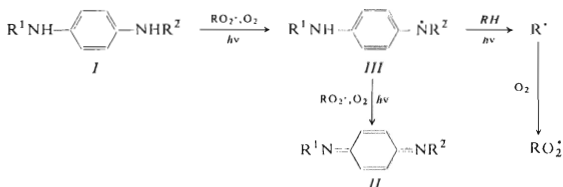
TABLE I

Photo-oxidation of squalane in the presence of derivatives of 1,4-phenylenediamine *I* and 1,4-benzoquinonediimine *II* (*c* concentration of additives, $5 \cdot 10^{-4} \text{ mol l}^{-1}$; λ 300–400 nm, 35°C, pressure of oxygen 0.1 MPa). Meaning of symbols and their dimensions *cf.* Experimental; *Ia* is standard

Additive	$\tau_{0.5}$	$\tau_{1.0}$	$\tau_{1.5}$	S_1	S_2	S_{r1}	S_{r2}
	10^3 s			10^{-8} s			
<i>Ia</i>	8.0	16.0	23.3	6.3	6.8	1.0	1.0
<i>Ib</i>	18.1	34.8	52.0	3.0	2.8	0.48	0.4
<i>Ic</i>	9.0	21.9	37.8	3.9	3.1	0.62	0.46
<i>IIb</i>	12.1	24.0	37.8	4.2	3.6	0.67	0.53
Control	27.4	45.8	60.8	2.7	3.4	—	—

from *I* (aminyl or nitroxide radicals) in the initiated initial stage of photo-oxidation. The initiation effect may play a more distinct role either in hydrocarbons which are oxidized more slowly or at a higher concentration of *I*. The lack of the induction period in the photo-oxidation also is a consequence of this effect. On the contrary, a pronounced induction period appears in the thermal oxidation¹ even at a very low concentration of *I*.

In the photo-oxidation of squalane, the saturated hydrocarbon, antioxidants *Ia–Ic* have a pro-oxidative effect. This is documented by both the τ and S_t values (Table I). The acceleration of oxidation is probably a result of the involvement of nitrogen-centered radical intermediates *III* originated from *I* in the photoinitiation process (Scheme 1). Benzoquinonediimine *Iib* also has a pro-oxidative effect, but experimental evidence which would explain the mechanism of its pro-oxidative properties is still lacking.



SCHEME 1

No induction period was observed in the photo-oxidation of tetralin stabilized with phenylenediamines *Ia–Ic* and *If*, even in the presence of high antioxidant concentrations (Table II). This is a difference from thermal oxidation where a quite pronounced induction period was observed in the presence of all the investigated amines¹. However, here at least the photo-oxidation process was effectively retarded from the very beginning, and in no case was the photo-oxidation accelerated. Differences in the retardative activity due to a change in the N,N'-disubstitution are of little importance and do not allow any discussion of the substituent effects. The efficiency is affected by the concentration at which the individual *I* are compared. Significant differences were observed in the effect of various derivatives of 1,4-phenylenediamine and 1,4-benzoquinonediimine applied at comparable molar concentration on the initial phases of the photo-oxidation of tetralin. This is why in some cases the $A_{t,1}$ values differ by as much as an order of magnitude (Tables II and III, Fig. 1). Values that can readily be correlated are found only at higher oxygen absorption values.

The retardative effect of most of *I* investigated here is distinctly affected by an in-

crease in the concentration of I only in the later stages of the process, after some 10 h of photo-oxidation. This can be seen in the stabilization of tetralin with $Ia-Ic$.

TABLE II

Photo-oxidation of tetralin in the presence of derivatives of 1,4-phenylenediamine (I); experimental conditions, meaning of symbols and standard arc the same as in Table I

Additive	c mol l^{-1}	$\tau_{0.5}$	$\tau_{1.0}$	$\tau_{1.5}$	A_{r1}	A_{r2}	S_1	S_2	S_{r1}	S_{r2}
		10^3 s					10^{-8} s			
<i>Ia</i>	$5 \cdot 10^{-4}$	12.6	28.8	40.5	1.0	1.0	3.1	4.3	1.0	1.0
	$1 \cdot 10^{-3}$	16.2	29.2	41.9	1.0	1.0	3.9	3.9	1.0	1.0
	$5 \cdot 10^{-3}$	16.9	32.4	50.4	1.0	1.0	3.2	2.8	1.0	1.0
	$1 \cdot 10^{-2}$	16.2	29.2	49.0	1.0	1.0	3.9	2.5	1.0	1.0
<i>Ib</i>	$5 \cdot 10^{-4}$	18.9	33.3	41.9	12.7	1.8	3.5	5.8	1.12	1.35
	$1 \cdot 10^{-3}$	14.0	31.1	54.8	0.5	1.3	2.9	2.1	0.75	0.54
	$5 \cdot 10^{-3}$	17.3	34.2	59.2	1.1	1.2	3.0	2.0	0.92	0.71
	$1 \cdot 10^{-2}$	16.2	39.6	64.6	1.0	2.8	2.1	2.0	0.55	0.8
<i>Ic</i>	$5 \cdot 10^{-4}$	20.6	39.1	50.2	15.8	2.9	2.7	4.5	0.87	1.04
	$1 \cdot 10^{-3}$	18.3	37.6	89.6	1.5	2.4	2.6	1.0	0.66	0.25
	$5 \cdot 10^{-3}$	15.5	32.8	61.0	0.7	1.0	2.9	1.8	0.9	0.63
	$1 \cdot 10^{-2}$	27.2	82.8	—	3.7	10.1	0.9	—	0.23	—
<i>If</i>	$5 \cdot 10^{-4}$	31.2	95.0	—	35.4	13.8	0.8	—	0.25	—
	$1 \cdot 10^{-3}$	46.8	144.0	—	8.4	20.5	0.5	—	0.13	—
Control	—	12.1	23.3	33.7	—	—	4.5	4.8	—	—

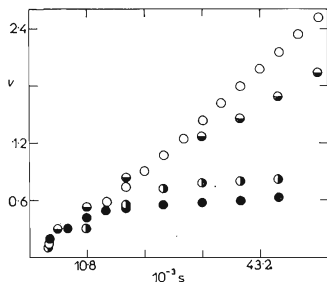


FIG. 1

Oxygen uptake, v ($\text{mmol O}_2/\text{mol}_{\text{substrate}}$), during the photo-oxidation of tetralin at 300–400 nm and 35°C in the presence of N,N' -diphenyl-1,4-benzoquinonediimine (*Ib*, concentration in mol l^{-1}): \circ 0, \bullet $5 \cdot 10^{-4}$, \circ $5 \cdot 10^{-3}$, \bullet $1 \cdot 10^{-2}$

Due to a more pronounced retardation of photo-oxidation in the later phase of the process, in some cases not even $1.0 \text{ mmol O}_2/\text{mol}_{\text{substr.}}$ uptake could be reached during the measurement. The result indicates some more complicated relations involved in the photo-oxidation of the system hydrocarbon/diamine *I*. Differences in the rate of photo-oxidation of the amines alone and in the rate of transformation of the primarily formed nitrogen-centered radical *III* are also probably involved.

Benzoquinonediimines *IIa–IIc* behave differently in the initial stage of photo-oxidation of tetralin (Table III). Experimental data indicate a weak pro-oxidative effect of *IIa* and *IIb* (Fig. 1). This effect becomes apparent only at a low concentration of the additive ($5 \cdot 10^{-4} \text{ mol l}^{-1}$), and after some 6 h it is converted to the retardative effect. The observed pro-oxidative effect of *IIa*, *IIb* cannot be interpreted unequivocally without a deep mechanistic study. Benzoquinonediimine *IIc* has no pro-oxidative effect. At higher concentrations of benzoquinonediimines *IIa*, *IIb* and *IId* the retardative effect gradually increases so that the rate of photo-oxidation is very low; and absorption as low as $1.0 \text{ mmol O}_2/\text{mol}_{\text{substrate}}$ could not be reached during the measurement (Fig. 1). It is of importance that the essential feature of the effect of all *II* investigated in this study is retardation of the later stage of photo-oxidation of tetralin. The S_r values are very similar for tetralin containing *I* and *II*. With respect to the proven^{17,18} conversion of *I* to *II*, the observed retardative effect can be explained through an active role of *II*.

The greatest importance for the characterization of the effect of derivatives of phenylenediamine on the photo-oxidation of rubbers has a model investigation carried

TABLE III

Photo-oxidation of tetralin in the presence of derivatives of 1,4-benzoquinonediimine (*II*); experimental conditions and meaning of symbols are the same as in Table I

Additive	c mol l^{-1}	$\tau_{0.5}$	$\tau_{1.0}$	$\tau_{1.5}$	A_{r1}	A_{r2}	S_1	S_2	S_{r1}	S_{r2}
		10^3 s					10^{-8} s			
<i>IIa</i>	$5 \cdot 10^{-4}$	8.8	25.4	42.1	—	0.4	3.0	3.0	0.97	0.69
	$5 \cdot 10^{-3}$	57.6	—	—	9.5	—	—	—	—	—
	$1 \cdot 10^{-2}$	36.0	—	—	5.8	—	—	—	—	—
<i>IIb</i>	$5 \cdot 10^{-4}$	10.1	23.6	40.5	—	0.1	3.7	3.0	1.19	0.69
	$5 \cdot 10^{-3}$	15.0	32.4	60.1	0.6	1.0	2.9	1.8	0.90	0.64
	$1 \cdot 10^{-2}$	15.0	—	—	0.7	—	—	—	—	—
<i>IIc</i>	$5 \cdot 10^{-4}$	26.0	—	—	2.9	—	—	—	—	—
	$1 \cdot 10^{-2}$	16.9	—	—	1.2	—	—	—	—	—
Control	—	12.1	23.3	33.7	—	—	4.5	4.9	—	—

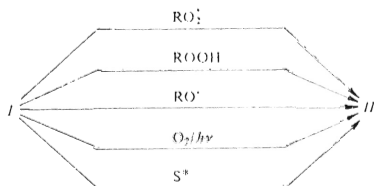
out in squalene. Already at the lowest concentration all derivatives of *I* used in the study retarded the photo-oxidation very strongly (Table IV). However, no induction period could be observed also in this hydrocarbon, even with *I* present at high concentrations (in the thermal oxidation¹, after 150 h the oxygen absorption was still quite insignificant in this case). The character of N,N'-disubstitution has no essential effect on the retardative activity of *I*. In the time interval taken for investigation (*i.e.*, up to 25 h), the retardative activity decreased in squalene in the presence of all the *I* with their increasing concentration. This finding indicates the role played by the pro-oxidative effect of reactive intermediates of the oxidation transformation of *I*. It is only the primary photo-oxidation product, *i.e.* the corresponding benzoquinone-dimine, that possesses a retardative effect, as shown in Table V.

TABLE IV

Photo-oxidation of squalene in the presence of derivatives of 1,4-phenylenediamine (*I*); experimental conditions, meaning of symbols and standard are the same as in Table I

Additive	c mol l^{-1}	$\tau_{0.5}$	$\tau_{1.0}$	$\tau_{1.5}$	A_{r1}	A_{r2}	S_1	S_2	S_{r1}	S_{r2}
		10^3 s					10^{-8} s			
<i>Ia</i>	$5 \cdot 10^{-4}$	13.4	20.9	27.7	1.0	1.0	6.7	7.3	1.0	1.0
	$1 \cdot 10^{-3}$	7.2	14.4	22.3	1.0	1.0	6.9	6.3	1.0	1.0
	$5 \cdot 10^{-3}$	8.5	15.4	21.2	1.0	1.0	7.3	8.5	1.0	1.0
	$1 \cdot 10^{-2}$	5.4	10.9	16.2	1.0	1.0	9.1	9.5	1.0	1.0
<i>Ib</i>	$5 \cdot 10^{-4}$	10.5	19.2	28.0	0.7	0.9	5.8	5.7	0.86	0.78
	$1 \cdot 10^{-3}$	7.6	14.0	20.4	1.1	0.94	7.8	7.8	1.13	1.24
	$5 \cdot 10^{-3}$	7.4	15.1	23.1	0.75	0.97	6.5	6.3	0.88	0.74
<i>Ic</i>	$5 \cdot 10^{-4}$	13.2	24.0	34.1	0.98	1.23	4.6	5.0	0.69	0.68
	$1 \cdot 10^{-3}$	6.0	11.8	19.2	0.63	0.64	8.7	6.7	1.26	1.07
	$5 \cdot 10^{-3}$	11.4	17.8	23.6	5.26	2.77	7.8	8.6	0.86	0.90
<i>Id</i>	$5 \cdot 10^{-4}$	6.4	14.3	21.8	0.26	0.53	6.3	6.7	0.94	0.92
	$1 \cdot 10^{-3}$	9.5	18.0	26.5	1.73	1.49	5.9	5.9	0.86	0.94
	$5 \cdot 10^{-3}$	13.1	23.4	31.1	2.02	1.96	4.9	6.5	0.67	0.77
	$1 \cdot 10^{-2}$	10.2	22.3	34.1	4.4	3.9	4.1	4.3	0.45	0.45
<i>Ie</i>	$5 \cdot 10^{-4}$	10.8	21.0	30.7	0.73	1.0	4.9	5.1	0.73	0.70
	$1 \cdot 10^{-3}$	7.9	16.2	26.5	1.22	1.24	6.0	4.9	0.88	0.77
	$5 \cdot 10^{-3}$	11.4	19.2	27.2	1.50	1.46	6.4	6.3	0.88	0.74
<i>If</i>	$5 \cdot 10^{-4}$	15.7	29.0	39.8	1.25	1.58	3.8	4.6	0.56	0.63
	$1 \cdot 10^{-3}$	4.8	9.0	13.2	0.25	0.27	11.9	11.9	1.72	1.89
	$5 \cdot 10^{-3}$	6.1	11.9	17.6	0.47	0.58	8.7	8.8	1.19	1.03
Control	—	4.0	7.0	8.7	—	—	16.5	29.2	—	—

All the investigated *Ila*–*Ild* not only retard the photo-oxidation of squalene more strongly than the derivatives of *I* used in an equimolar concentration: their retardative effect becomes stronger with concentration, according to the results obtained with *Ila* and *Ilc*. This result is in keeping with the pro-oxidative effect of intermediates arising from *I* as considered above (they cannot become operative if *II* is directly added to the oxidized hydrocarbon) and indicates that *II* itself does not participate in the initiation process and that it is capable of deactivating the chain-propagating radicals R^\cdot , RO_2^\cdot or the chain-branching radicals RO^\cdot . Deactivation of radiation in the range of the wavelengths used (300–400 nm) can also be observed, *i.e.*, a screening



SCHEME 2

TABLE V

Photo-oxidation of squalene in the presence of derivatives of 1,4-benzoquinonediimine (*II*); experimental conditions, meaning of symbols and standard are the same as in Table I

Additive	c mol l ⁻¹	$\tau_{0.5}$	$\tau_{1.0}$	$\tau_{1.5}$	A_{r1}	A_{r2}	S_1	S_2	S_{r1}	S_{r2}
		10 ³ s					10 ⁻⁸ s			
<i>Ila</i>	$5 \cdot 10^{-4}$	10.1	17.3	30.0	0.65	0.74	6.9	4.0	1.04	0.54
	$1 \cdot 10^{-2}$	9.9	25.0	40.8	4.2	4.6	3.3	3.2	0.37	0.33
	$5 \cdot 10^{-3}$	23.2	45.7	73.1	—	—	2.2	1.8	—	—
<i>Ilb</i>	$5 \cdot 10^{-4}$	15.6	28.9	44.3	1.24	1.58	3.8	3.3	0.56	0.45
	$1 \cdot 10^{-2}$	18.0	31.4	46.3	9.94	6.26	3.7	3.4	0.41	0.35
<i>Ilc</i>	$5 \cdot 10^{-3}$	19.7	49.0	82.8	3.46	5.04	1.7	1.5	0.23	0.17
<i>Ild</i>	$5 \cdot 10^{-4}$	13.9	21.5	30.0	1.06	1.04	6.6	5.9	0.99	0.80
	$1 \cdot 10^{-3}$	16.8	29.2	38.1	4.0	3.0	4.1	5.6	0.6	0.90
Control	—	4.0	7.0	8.7	—	—	16.5	29.2	—	—

photostabilizing effect of benzoquinonediimines. This is a consequence of their ability to absorb radiation in the range of longer wavelengths than do the derivatives of 1,4-phenylenediamine (for λ_{\max} see Experimental).

The results of measurements carried out in this study pointed out unambiguously the weak antioxidative efficiency of derivatives of 1,4-phenylenediamine *I* in the photo-oxidation of hydrocarbons (RH). 1,4-Phenylenediamines *I* used are oxidized to 1,4-benzoquinonediimines *II* by several parallel routes operative to various degree (Scheme 2). Only part of these transformation mechanisms contribute to the active role of *I* in the chain-breaking process.

The transformation of *I* proceeds with the participation of radicals RO_2^{\cdot} and hydroperoxides (formed in the propagation stage of oxidation, the latter also in the oxidation of unsaturated hydrocarbons with singlet oxygen), radicals RO^{\cdot} (formed by the photolysis of ROOH), and of molecular oxygen in the ground state. By analogy with the photo-oxidation of aliphatic amines (e.g., ref.²¹), the active participation of sensitizers in the excited triplet state (s^*) must also be taken into account in the formation of nitrogen-centered radicals and in their subsequent transformation into *II*. Carbonyl compounds arising by transformations of ROOH in the oxidation of polymeric hydrocarbons may also become such sensitizers, even though to a limited extent. Owing to the short length of the kinetic chain in the photo-oxidation connected with the fast generation of radicals RO_2^{\cdot} and RO^{\cdot} and at the simultaneous high concentration of molecular oxygen the transformation of *I* due to these agents is a favoured process. The observed resulting effect on the photo-oxidation is a consequence of the fast formation of *II* accumulated in the hydrocarbon and possessing a retardative effect.

REFERENCES

1. Rotschová J., Pospíšil J.: This Journal 47, 2501 (1982).
2. Dunn J. R.: Trans. Inst. Rubber Ind. 34, 20 (1958).
3. Dunn J. R.: J. Appl. Polym. Sci. 4, 151 (1960).
4. Ellison D. H., Salmon G. A., Wilkinson F.: Proc. Roy. Soc. London, Ser. A, 328, 23 (1972).
5. Bensasson R. V., Thomas J. K.: Int. J. Radiat. Phys. Chem. 1, 185 (1969).
6. Monet J. C., Reverdy G.: J. Chem. Soc., Chem. Commun. 1982, 654.
7. Maeda K., Nakane A., Tsubomura H.: Bull. Chem. Soc. Japan 48, 2448 (1975).
8. Linschitz H., Ottolenghi M., Bensasson R. V.: J. Amer. Chem. Soc. 89, 4952 (1967).
9. Linschitz H., Rennert J., Korn T. M.: J. Amer. Chem. Soc. 76, 5839 (1954).
10. Fitzgerald E. A., Wuelving P., Richtol H. H.: J. Phys. Chem. 75, 2737 (1971).
11. Canva G. P., Canva J. J.: Rubber J. 153, 36 (1971).
12. Dalle J. P., Magons R., Mousseron-Canet M.: Photochem. Photobiol. 15, 411 (1972).
13. Young R. H., Martin R. L., Feriozi D., Brewer D., Kayser R.: Photochem. Photobiol. 17, 233 (1973).
14. Carlsson D. J., Wiles D. M.: Rubber Chem. Technol. 47, 991 (1974).
15. Saito I., Abe S., Takahashi Y., Matsuura T.: Tetrahedron Lett. 1974, 4001.

16. Manring L. E., Foote C. S.: *J. Phys. Chem.* **86**, 1257 (1982).
17. Rotschová J., Pospíšil J.: *Chem. Ind. (London)* **1981**, 393.
18. Rotschová J., Pospíšil J.: *J. Chromatogr.* **211**, 299 (1981).
19. Boozer C. E., Hammond G. S.: *J. Amer. Chem. Soc.* **76**, 3861 (1954).
20. Goda K., Tanaka M., Murata N.: *J. Appl. Polym. Sci.* **15**, 403 (1971).
21. Davidson R. S., Trethewey K. R.: *J. Chem. Soc., Perkin Trans. 2*, **1977**, 169, 173.

Translated by L. Kopecká.