Primary Processes of Stabilizer Action in Radiation-induced Alkane Oxidation

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Results of pulse-radiolytic model experiments on the auto-oxidation of long-chain n-alkanes and auto-oxidation retardation are presented. In pure n-heptadecane and solutions of di-t-butyl-*p*-cresol or diphenylamine the reaction of alkyl radicals with oxygen and the corresponding competition reactions with the stabilizer prototypes have been characterized by spectroscopic and kinetic data. A reaction mechanism describing the radiation-induced processes within the system long-chain n-alkane-oxygen-stabilizer is discussed.

Oxidation and auto-oxidation are interesting aspects for the practical use of low- and high-molecular weight hydrocarbons as cooling and insulator oils, as cable insulation materials and for many purposes of polyolefin application.^{1, 2} The oxidation process can be induced by different pathways which all result in the generation of free radicals. Pyrolysis, photolysis and radiolysis of alkanes yield mainly alkyl radicals (R') and subsequent products (allyl radicals *etc.*). The alkyl radicals react rapidly with oxygen to form peroxy radicals:

$$\mathbf{R}^* + \mathbf{O}_2 \to \mathbf{ROO}^*. \tag{1}$$

These can decay by slow H-abstraction [reaction (2)] or bimolecularly [reaction (3)]:

$$ROO' + RH \rightarrow R' + ROOH$$
(2)

$$2\text{ROO}^{\bullet} \rightarrow \text{RO}_{4}\text{R} \rightarrow 2\text{RO}^{\bullet} + \text{O}_{2}.$$
(3)
tetroxide

Hydroperoxides are formed as products of reaction (2). Depending on temperature or the presence of catalysts and impurities peroxides decompose mainly to oxy radicals, which are also the initiating species of the classical peroxide-induced polymerization

$$\operatorname{ROOH} \xrightarrow{\Delta, \operatorname{catalyst}} \operatorname{RO'} + \operatorname{OH}.$$
(4)

The bimolecular reaction (3) also forms oxy radicals via the unstable tetroxide.

The oxy radicals play a key role in the oxidation chain because they can regenerate alkyl radicals

$$RO' + RH \to ROH + R' \tag{5}$$

and can decay by different reaction channels such as disproportionation, recombination and fragmentation:³

$$2RO' \xleftarrow{ROH + R'HC=O}_{fragments.}$$
(6)

Hence, the RO' decay [reactions (5) and (6)] forms stable oxidation products and also regenerates the initiating species R'.

To prevent or to retard the oxidative degradation stabilizers are added to the alkane system.⁴ These stabilizers may act in very different ways, *e.g.* by preventing alkyl radical

formation by quenching their precursor states; by reaction with the radicals that take part in the single steps of the oxidation, forming stable, unreactive species and by deactivation of substances catalysing the hydroperoxide decomposition [reaction (4)]. Most stabilizers have a complex effect, depending very much on the reaction conditions of temperature, concentration and mobility of the reactants.

The diversity of stabilizers against oxidation encompasses chain-breaking substances (intercepting the reactive intermediates), metal-ion deactivators and peroxide decomposers (in the sense of generation of stable products). Chain-breakers are generally used in practice. These substances act either as traps for free radicals (*e.g.* quinones), as electron donors (*e.g.* tertiary amines) or as hydrogen donors (*e.g.* secondary aryl amines and hindered phenols). The use of the last type is predominant and they work by cleaving a labile N—H or O—H bond and by conversion of the reactive transients R^{*} and RO^{*}₂ into relatively stable products according to the reactions

$$Ar_{2}NH + R' \rightarrow Ar_{2}N' + RH$$
(7)

$$Ar_2NH + RO_2^{\bullet} \rightarrow Ar_2N^{\bullet} + ROOH$$
(8)

$$ArOH + R' \to ArO' + RH \tag{9}$$

$$ArOH + RO_2^{\bullet} \rightarrow ArO^{\bullet} + ROOH$$
(10)

where Ar denotes an aromatic ring.

The fate of the less-reactive Ar_2N' and ArO' radicals is determined by bimolecular reactions such as⁴

$$Ar_2N' + ROO' \to Ar_2NO_2R \tag{11}$$

$$ArO' + ROO' \rightarrow ROOArO.$$
 (12)

The knowledge of these reactions originates mainly from steady-state experiments. Still to be studied are the selectivity of the formulated elementary reactions, exact kinetic data and a critical consideration of the different reaction paths in liquid and solid (polymer) states. Therefore, the aim of the investigations presented in this paper was to try for a direct time-resolved kinetic analysis of hydrocarbon oxidation and its re-tardation in presence of stabilizers. As model hydrocarbons, two long-chain n-alkanes $(n-C_{16}H_{34} \text{ and } n-C_{17}H_{36})$ were chosen and as stabilizers the prototypes of amine and phenolic stabilizers, diphenylamine and di-t-butyl-*p*-cresol (ionol), were used.

Electron pulse radiolysis was used for the generation of alkyl radicals. The experiments consisted of the stepwise investigation of pure n-alkanes, the alkane-oxygen system and the system alkane-oxygen-stabilizer.

Experimental

The solutions were irradiated with 40 ns, 100 Gy (in H_2O) pulses of 1 MeV electrons from an Elit accelerator. The optical detection system consisted of a pulsed xenon lamp, a high intensity grating monochromator and a photomultiplier 1 P 28. The signals were fed into a 500 MHz real-time oscilloscope. Further details are given in ref. (5) and (6).

To remove unsaturated impurities and branched alkanes n-hexadecane and n-heptadecane (VEB Chemische Fabrik Erkner) were treated 5 times with 60% oleum. After washing with water and drying, the alkanes were passed through columns filled with molecular sieves A4 and X13.

Diphenylamine (VEB Laborchemie Apolda) and di-t-butyl-p-cresol (Bayer Leverkusen) were purified by chromatography over Al_2O_3 using cyclohexane as solvent.

Before irradiation the samples were bubbled for 15 min with purest grade Ar or with Ar-O₂ mixtures prepared in a water-tight gasometer. The oxygen saturation concentration in the alkanes was determined as $c_{o_2} = 1.25 \times 10^{-2}$ mol dm⁻³ at 25 °C. During the



Fig. 1. Transient spectra in n-hexadecane taken in the time profile maximum for oxygen-free and oxygen-containing samples: \times , Ar-bubbled; \blacktriangle , 7.4×10^{-4} mol dm⁻³ O₂; \bigcirc , O₂-saturated (1.25 $\times 10^{-2}$ mol dm⁻³ O₂).

experiment the sample flowed in a cycle consisting of the irradiation cell and the degassing vessels to minimize radiolysis products within the investigation layer.

Results

n-Alkane – Oxygen System

Fig. 1 and 2 show spectra obtained immediately after a 40 ns electron pulse in $n-C_{16}H_{34}$ and $n-C_{17}H_{36}$, respectively. In both cases a long-lived absorption tail was observed, which decayed towards longer wavelengths. The virtual maximum at the u.v. border may be caused in some part by the influence of scattering light. These absorptions are interpreted by analogy findings in cyclohexane^{7,8} as being due to the sum of absorption of different alkyl radicals derived from the long-chain n-alkanes. Because of the long pulse and the relatively high dose per pulse compared with earlier experiments practically no cation and electron absorptions could be found.

In the presence of oxygen the radical absorption tail shifted towards longer wavelengths. At low oxygen concentrations ($< 10^{-3} \text{ mol dm}^{-3}$) a growth in absorption superimposed on the alkyl radical decay was observed in the time profiles (fig. 3 and 4). The spectra of the new transient taken at the time profile maxima, however, do not depend markedly on oxygen concentration. These experimental findings and the analogy with spectroscopic data obtained in other hydrocarbon and alcohol-oxygen systems^{3, 7} identify the oxygen-dependent transient as the alkylperoxy radical derived from the sum of the isomer alkyl radicals.

The decay kinetics of the peroxy radical could be analysed at $\lambda = 270$ nm where the

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Fig. 2. Transient spectra in n-heptadecane taken in the time profile maximum: \times , Ar-bubbled; \blacktriangle , 7.4 × 10⁻⁴ mol dm⁻³ O₂; \bigcirc , 1.6 × 10⁻³ mol dm⁻³ O₂.



Fig. 3. Time profiles in n-hexadecane at $\lambda = 270$ nm in Ar-saturated (\bigcirc) and oxygen containing samples: \times , 7.4 \times 10⁻⁴; \bigcirc , 1.3 \times 10⁻³; \triangle , 3.1 \times 10⁻³; and \blacksquare , 1.25 \times 10⁻² mol dm⁻³ O₂.

ROO' adsorption is more than twice that of R' (cf. arrow in fig. 1). From simple firstorder plots using the time profiles given in fig. 3 and 4 a rate constant for ROO' formation [eqn (1)] of $k_1 = 1.5 \times 10^9$ dm³ mol⁻¹ s⁻¹ was determined that agrees well with peroxy radical formation of alcohol radicals determined from competition kinetics.¹⁰

The plotted rate constant value was confirmed by fitting numerically the experimental



Fig. 4. Time profiles in n-heptadecane at $\lambda = 270$ nm in Ar-saturated (\bullet) and O₂-containing samples: \times , 7.4 \times 10⁻⁴; \bigcirc , 1.3 \times 10⁻³ and \triangle , 3.1 \times 10⁻³ mol dm⁻³ O₂.

points according to the method of Runge-Kutta with the following set of differential equations as shown in fig. 3 and 4 by the lines

$$\frac{\mathrm{d}[\mathbf{R}^{\cdot}]}{\mathrm{d}t} = g(t) - k_1[\mathbf{R}^{\cdot}][\mathbf{O}_2] - k_y[\mathbf{R}^{\cdot}] \tag{I}$$

$$\frac{\mathrm{d}[\mathrm{ROO'}]}{\mathrm{d}t} = k_1[\mathrm{R'}][\mathrm{O}_2] - k_x[\mathrm{ROO'}] \tag{II}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}(X_{\mathrm{obsd}}) = \frac{\mathrm{d}[\mathbf{R}^{\,\prime}]}{\mathrm{d}t}\varepsilon l + \frac{\mathrm{d}[\mathbf{ROO}^{\,\prime}]}{\mathrm{d}t}\varepsilon l \tag{III}$$

g(t) represents generation by a 40 ns right-angle pulse according to [reaction (13)], k_x and k_y are the experimentally observed non-specific decays of the transients by recombination or reaction with impurities, X_{obsd} is the observed total absorbance at the analysing wavelength, ε is the transient extinction coefficient and l is the optical pathlength.

Reactions with the Phenolic Stabilizer

In the presence of di-t-butyl-*p*-cresol (DBC) the u.v. part of the spectrum ≤ 280 nm is masked. Fig. 5 shows transient spectra obtained from time-profile maxima after pulsing various concentrations of DBC in deaerated n-heptadecane. Even at $c_s = 10^{-3}$ mol dm⁻³ an absorption peak with a maximum at 300–310 nm could be observed. This is assigned by comparison with flash photolysis experiments to be due to the phenoxy radical.¹¹ This peak grows considerably with increasing concentration and at $c_s = 10^{-2}$ mol dm⁻³ a further maximum appears with $\lambda_{max} = 350-360$ nm, which is proposed to be a cyclohexadienyl-type radical analogous to those found in ref. (12) and (13). The formation of the first peak could be followed by time-resolved measurements as demonstrated in fig. 6. Because of a very intense fluorescence the rising absorption is distorted. From plots of the residual growth and a simple fit operation using the differential equations (IV) and (V) a rate constant of $k_9 = 8 \times 10^8$ dm³ mol⁻¹ s⁻¹ was estimated:

$$\frac{\mathrm{d}[\mathrm{R}^{\,\prime}]}{\mathrm{d}t} = g(t) - k_{9}[\mathrm{R}^{\,\prime}][\mathrm{DBC}] - k_{y}[\mathrm{R}^{\,\prime}] \tag{IV}$$

$$\frac{\mathrm{d}[\mathrm{DBC}^{\cdot}]}{\mathrm{d}t} = k_{9}[\mathrm{R}^{\cdot}][\mathrm{DBC}] - k_{x}[\mathrm{DBC}^{\cdot}]. \tag{V}$$



Fig. 5. Transient spectra taken in the time profile maximum in deaerated solutions of DBC in n-heptadecane: ×, 10⁻³; ●, 10⁻²; □, 2×10⁻²; ●, 5×10⁻² and △, 0.1 mol dm⁻³ DBC.



Fig. 6. Time profiles at $\lambda = 290$ nm of deaerated solutions of DBC in n-heptadecane: \bigcirc , 10^{-3} ; \bigcirc , 3×10^{-3} ; \bigcirc , 10^{-2} ; \Box , 0.1 mol dm⁻³ DBC.



Fig. 7. Time profiles at $\lambda = 360$ nm of a solution of 0.1 mol dm⁻³ DBC in n-heptadecane: ×, deaerated; •, 4×10^{-3} mol dm⁻³ O₂; \triangle , O₂-saturated.

In this case no transient superposition was taken into account.

In the presence of oxygen the formation of the phenoxy radical became much faster, indicating competition between oxygen and DBC for the precursor species. This was confirmed also by the 40% lower transient yield at $c_{\rm DBC} = 0.1 \text{ mol dm}^{-3}$ in the presence of O₂, whereas the decay behaviour seems not to be influenced markedly.

The second peak transient ($\lambda_{max} = 360 \text{ nm}$) shows no time-resolved generation and seems to be formed in competition with a fast reaction. In oxygen-saturated solutions it is depressed to *ca*. 40% and the lifetime is reduced to *ca*. 800 ns, as demonstrated in fig. 7. From the lifetime reduction in the presence of O₂ a rate constant of $k_{20} = 9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was calculated [reaction (20) in table 1].

Reactions with Diphenylamine

The analysis of radical processes proceeding within the system n-alkane – diphenylamine (DPA)–oxygen only could be analysed in regard to the reactions in the phenolic system described before. Fig. 8 shows the end-of-pulse transient spectrum obtained in an Arbubbled solution of 10^{-2} mol dm⁻³ DPA in n-heptadecane. Three peaks can be distinguished with maxima at 310, 380 and 520 nm which, for kinetic reasons, should be due to different species.

The 310 nm peak showed a time-resolved formation at low DPA concentration that became faster and narrower in the presence of oxygen (*cf.* fig. 9). At $c_{\text{DPA}} = 10^{-2}$ mol dm⁻³ the absorption grows within the pulse. In the presence of oxygen 40% (4×10^{-3} mol dm⁻³ O₂) to 50% (O₂-saturated) of the transient absorption decayed rapidly, indicating a superposition of two reactive species at this wavelength (fig. 10).

The kinetic behaviour of this very oxygen-sensitive part of the 320 nm absorption agrees well with that of the 520 nm one. Their original half-life of *ca*. 800 ns is independent of c_{DPA} and is reduced by oxygen owing to a pseudo-first-order reaction with a rate constant $k = (2.0 \pm 0.5) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (cf. fig. 11). From this behaviour and in comparison with laser flash-photolysis experiments with other secondary and tertiary

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of DBC	remarks	time-resolved ^{a,b} from transient depletion in the presence of O_2	fast formation ^a [competition reactions (14), (15) and (19)] no indication under conditions of PR with optical detection	
ned in the presence	$k/\mathrm{dm}^3 \mathrm{mol}^{-1} \mathrm{s}^{-1}$	8 × 10 ⁸ ca. 10 ⁹	ca. 10° 9 × 107	
f transients forn	reaction no.	(9) (18)	(19) (20) (10)	Ref. (11).
spectroscopic and kinetic properties o	reactions	R`+ArOH → RH+ArO` H+ArOH → H ₂ +ArO`	H+ArOH → HAr'OH HAr'OH+0, → (HArOO')OH ROO'+ArOH → ROOH+ArO'	^a This work. ^b
Table 1. S	$\lambda_{ m max}/ m nm$	300	350-360	
	transient	cH ₃ -0.	CH ₃ CH ₃ OH	

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Fig. 8. Transient spectra taken in the time profile maximum in a solution of 10^{-2} mol dm⁻³ DPA in n-heptadecane: ×, deaerated; \bigcirc , 4.2×10^{-3} mol dm⁻³ O₂; \triangle , 1.25×10^{-2} mol dm⁻² mol dm⁻³ O₂; (--) cyclohexadienyl-type radical as difference spectrum between O₂-free and O₂-containing sample; •, spectrum of species decaying in 300 ns in a sample containing 4.2×10^{-3} mol dm⁻³ O₂ (see also fig. 10).

phenylamines¹⁴ the transient is assigned to the DPA triplet which besides the 520 nm peak also has a considerable absorption at 310 nm. The transient spectrum can be obtained roughly from the difference between maximum time-profiles (immediately after the pulse) and the absorptions 300 ns after the pulse in oxygen-containing solution (*cf.* fig. 8).

The kinetics of the 380 nm species is rather complex: e.g. at $c_{DPA} = 5 \times 10^{-2}$ mol dm⁻³ fast and time-resolved absorption parts could be observed. The fast part was depressed with decreasing concentration. The time-resolved part, however, could be observed even at $c_{DPA} = 10^{-3}$ mol dm⁻³ and its formation seems to be connected with the DPA^T (triplet) decay. This is demonstrated in fig. 12. Also the oxygen influence on the time profiles of the 520 and 380 nm transients (fig. 12) confirms the decay–formation relationship between both transients. From these kinetic observations and in analogy to observations made in similar substituted aromatic systems, such as dimethylaniline¹² and aromatic olefins,^{13, 15} the 380 nm transient is interpreted to be a cyclohexadienyl-type radical.



Fig. 9. Time profiles at $\lambda = 320$ nm in a 10^{-3} mol dm⁻³ solution of DPA in n-heptadecane: \triangle , O₂-free; ×, 4×10⁻³ mol dm⁻³ O₂.



Fig. 10. Time profiles at $\lambda = 320$ nm in a 10^{-2} mol dm⁻³ solution of DPA in n-heptadecane: \triangle , O₂-free; ×, 4×10⁻³ mol dm⁻³ O₂; •, O₂-saturated; \triangle , difference due to competition of reaction (16).

Discussion

Spectroscopic investigation of some alcohol and hydrocarbon radicals and their corresponding peroxy radicals was one of the earliest studies using the pulse radiolysis technique.¹⁶ In the case of alkane oxidation the cyclic compounds such as cyclohexane and cyclopentane have been investigated intensely^{7, 8} probably because of the betterdefined structure of the radicals they generate compared with n-alkanes.

For n-alkanes a sum of isomeric radicals located in final and central chain position is always expected. Therefore, all our spectroscopic and kinetic data are mean values



Fig. 11. Time profiles at $\lambda = 520$ nm in solutions of \bigcirc , 10^{-3} mol dm⁻³ DPA (O₂-free) and 10^{-2} mol dm⁻³ DPA [×, O₂-free; \triangle , 4×10^{-3} mol dm⁻³ O₂] in n-heptadecane.



Fig. 12. Time profiles at $\lambda = 500$ nm (×) and $\lambda = 380$ nm (\triangle) of solutions of 5×10^{-2} mol dm⁻³ DPA (containing 10^{-3} mol dm⁻³ O₂) (----) and 10^{-2} mol dm⁻³ DPA (---) in n-heptadecane.

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owing to the sum of these species. Nevertheless, we undertook pulse radiolysis experiments with the long-chain n-alkanes $n-C_{16}H_{34}$ and $n-C_{17}H_{36}$. As described above the absorption tails of alkyl and alkylperoxy radicals R' and ROO' were observed. The mean rate constant for ROO' formation [reaction (1)] was $k_1 = 1.5 \times 10^9$ dm³ mol⁻¹ s⁻¹. The spectroscopic and kinetic data of the alkane-oxygen system are collected in table 2.

In the following discussion interest will be focussed on the possibility of analysing reactions of \mathbf{R}^{\cdot} and also other simultaneously radiation-generated transients such as H radicals and electronically excited molecules with the model stabilizers DBC and DPA.

DBC

DBC acts as an effective radical scavenger. Its reactions with the primary species generated in the alkane are summarized in table 1. Both radical transients R[•] and H react with the labile O—H bond of DBC, forming phenoxy radicals, but most of these radicals originate from the reaction with the alkyl radicals [reaction (9)]. This can be explained by the fast competition of reactions (14) and (15) with reaction (18) and, hence, a considerable part of R[•] is delivered subsequently by the H-abstraction [reaction (14)].

The cyclohexadienyl-type radicals (radical addition to the aromatic ring) could be observed only at higher DBC concentration as species formed immediately during the pulse. Obviously, the alkyl radicals are not added to the aromatic ring for reactivity and steric reasons. Thus the transient is formed only by addition of H [reaction (19)] in competition with reactions (14) and (15).

In the presence of oxygen further competition [reaction (16)] brings about the depletion of the cyclohexadienyl radicals and also a faster decay owing to peroxy radical formation [reaction (20)].

Reactions of the alkylperoxy radicals with DBC could not be observed under our experimental conditions. From the literature, however, it is known that such reactions are very slow and therefore represent the rate-determining step in the auto-oxidation chain.²⁰ Finally, no reaction of the phenoxy radicals with oxygen could be found.

DPA

In the case of DPA the reaction events are more complicated than those observed with DBC. This can be seen even in analysis of the absorption spectra. As shown in fig. 8 the transient absorption spectrum taken immediately after the pulse represents a superposition of the absorptions of the amine radical Ar_2N' , the cyclohexadienyl radical $HAr_2'NH$ and the triplet DPA^T. On the basis of the oxygen-scavenger reaction and considering the different reactivities the different transient absorptions can be separated and characterized. In table 3 are given the spectroscopic and kinetic data of these species.

For reactions of the alkyl radicals with DPA there is only evidence for H-abstraction [reaction (7)] from the labile N—H bond. Besides this mean formation path of Ar_2N a small part of this species seems to be formed also by the non-specific H-reaction [reaction (21)].

The generation of cyclohexadienyl-type radicals proceeds by two paths: by H-addition to the aromatic ring [reaction (23)] and by the reaction of the amine triplet with the solvent. The first reaction is included in the fast part of the transient growth, while the second is time-resolved and independent of amine concentration. As in case of DBC, for DPA no reaction with alkylperoxy radicals could be found.

The formation of the DPA^T proceeds by singlet energy transfer from the alkane to the amine and subsequent fast intersystem crossing. The existence of DPA^T even at $c_{\text{DPA}} = 10^{-3} \text{ mol dm}^{-3}$ may be explained in spite of the short RH^s lifetime by the relatively long electron pulse and a further generation source, *viz*. the direct radiative formation of DPA^s by RH^s fluorescence and Čerenkov light.

	Table 2. S _l	pectroscopic and kinetic properties of	transients forme	d in the system n-C	$C_{17}H_{36}-O_2$
transient	$\lambda_{\max}/nm_{\perp}$	reactions	reaction no.	$k/dm^3 mol^{-1} s^{-1}$	remarks
R. ROO:	≤ 240 ≤ 250	RH ~→ R', H', RH ^s R'+0 → ROO'	(13)	${1.5 \times 10^9}$	8
H	007	$H + RH \rightarrow R' + H_2$	(14)	$ca. 5+10^{7}$	estimated in analogy to literature ^b
		$2H \rightarrow H_2 \\ H + O \rightarrow HOO$	(15)	2×10^{10} 1.2 × 10^{10}	in water ^c in water ^c
RH ^s	≤ 210	$RH^{S} \rightarrow RH + hv$	(11)	$2 \times 10^{8} \text{ s}^{-1}$	emission ^d
		$ROO + RH \rightarrow ROOH + R$	(30)	$10^{0}-10^{2}$	steady-state expt ^e
		^a This work. ^b Ref. (17). ^c Ref. (18). ^a Ref. (19).	r Ref. (20).	
		Table 3. Spectroscopic and kineti	c data of the DI	A transients	
transient	$\lambda_{ m max}/ m nm$	reactions	reaction no.	k/s^{-1}	remarks
Ar_2N .	310	$\begin{array}{l} \mathbf{R}^{\cdot}+\mathbf{Ar}_{2}\mathbf{NH}\rightarrow\mathbf{Ar}_{2}\mathbf{N}^{\cdot}+\mathbf{RH}\\ \mathbf{H}+\mathbf{Ar}_{2}\mathbf{NH}\rightarrow\mathbf{Ar}_{2}\mathbf{N}^{\cdot}+\mathbf{H}_{2}\end{array}$	(7) (21)	≤ 10 ⁹ ca. 10 ⁹	superimposed with T-absorption ^{a,b} indirect from O_a -influence
INH-Ar	380	Ar₂N' + O₂ → Ar₂NOO' H + Ar₂NH → HAr'NHAr	(22) (23)	$\leq 10^7$ ca. 2×10^9	fast absorption part [competition reactions (14). (15) and (23)] ^{4,6}
]		$Ar_{s}NH^{T} + RH \rightarrow HAr'NHAr + R'$ $HAr'NHAr + O_{s} \rightarrow$ $HAr'ONHAr + O_{s} \rightarrow$	(24) (25)	2×10^6 10^8	
Ar_2NH^T	520	$\begin{array}{c} \mathbf{R}^{\mathrm{HALOO}}_{\mathrm{NH} \to \mathrm{RAr}^{\mathrm{NHAr}}} \\ \mathbf{R}^{\mathrm{H}}_{\mathrm{S}} + \mathbf{A}_{\mathrm{S}}^{\mathrm{NH} \to \mathrm{RAr}^{\mathrm{NH}}} \\ \mathbf{R}^{\mathrm{H}}_{\mathrm{S}} + \mathbf{R}_{\mathrm{S}}^{\mathrm{H}} \\ \mathbf{N}^{\mathrm{H}}_{\mathrm{S}} + \mathbf{N}^{\mathrm{H}} \end{array}$	(26) (27)	ca. 8×10^{9}	not observed k extrapolated ^{a, d}
	920	$Ar_{s}^{NH^{T}} \rightarrow Ar_{s}^{NH^{T}}$ $Ar_{s}^{NH^{T}} + RH \rightarrow see above$ $Ar_{s}^{NH^{T}} + O_{s} \rightarrow Ar_{s}^{NH} + O_{s}$ $ROO' + Ar_{s}^{NH} \rightarrow ROOH + Ar_{s}^{N}N'$	(28) (29) (8)	2 × 10 ⁹	ø ca. 0.8 no indication under our expt
		^a This work. ^b Ref. (14). ^c	Ref. (13). ^a Ref	. (19).	conditions

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Apart from solvent reaction [reaction (24)] and the oxygen reaction [reaction (29)], no indication for DPA^T decay by isomerization to a dihydrocarbazol triplet (as reported in the literature mainly for N-substituted diphenylamines²²) was found.

Using scheme 1 we tried to illustrate the complex connections of the radiation-induced processes in the system n-alkane-diphenylamine-oxygen. The species directly observed by pulse radiolysis are marked by circles. Reactions which could be characterized kinetically in this paper are indicated by bold lines.

Because of the relatively short lifetimes of the alkane singlet RH^s ($\tau \approx 5.0$ ns) and the DPA^s ($\tau \approx 3.6$ ns) under the described experimental conditions, no marked influence of oxygen on the generation of the electronically excited amine singlet and triplet state was observed.



product 1: hydrocarbon oxidation products, *e.g.* ROOH, ROH, R'CO— *etc.* product 2: recombination and isomerization products product 3: oxidation products of the amine

Reactivity of the Radicals

On the basis of the rather limited data contained in this paper we will try to formulate some reactivity statements.

Both stabilizers (DBC and DPA) react with the alkyl radicals only at the labile O-H or N-H bond. Hydrogen radicals are normally transformed to alkyl radicals by H-abstraction from the alkane [reaction (14)]. At higher stabilizer concentration they take part in reaction with it in a non-selective way, *i.e.* by reaction with the N-H and O-H and by addition to the aromatic ring.

Excited molecular triplet states (T states) may be efficient for reactions even at low stabilizer concentration and react with the solvent by H-abstraction, forming cyclo-hexadienyl-type radicals preferentially. In each case the oxygen concentration determines the product distribution, but the main reaction of the alkyl radicals with the labile H atoms of the stabilizer is predominant.

For all stabilizer radicals except ArO', reactions with the oxygen were observed that were generally slower than those of alkyl radicals [eqn (1)].

The decay of alkylperoxy radicals by recombination [eqn (3)], solvent reaction [eqn (2)] and stabilizer reaction [eqn (8) and (10)] could not be observed using pulse

radiolysis and optical spectroscopy. For this reason experiments using time-resolved e.s.r. spectroscopy are in preparation.²¹ Investigation of oxy radical reactions as outlined by eqn (5) and (6) is impossible at present using our techniques.

General Mechanistic Considerations

The experiments presented here should be understood as model investigations in several sizes.

The first aspect is a test for the ability to describe the kinetics and mechanism of auto-oxidation and its retardation on the basis of direct time-resolved experiments. This point has a distinct importance for the liquid-phase oxidation of hydrocarbons even if really practical conditions are given in more complex systems and at higher temperatures.

A further point of view is making model experiments for polymer (PE) oxidation and, particularly, for polymer stabilization. In this case it is necessary to have exact data on the possible transients because a kinetic identification in the highly viscous state is rather difficult. Such time-resolved experiments are in preparation.

A third aspect is a consideration on the general stabilizer action in oxidizing hydrocarbon systems. Based on a wide spectrum of steady-state experiments with different initiation methods most attention is focussed on the reaction of alkylperoxy radicals with the stabilizer, *e.g.* reactions (8) and (10), that is interpreted as the efficient termination step.

In the liquid phase except during preparative oxidations, *i.e.* under conditions of normal use of hydrocarbons, because of the rediffusion of oxygen, the slow reaction of ROO' with the stabilizer [reaction (8) and (10)] and the relatively high stabilizer concentration used (*ca.* 10^{-2} mol dm⁻³) this consideration should be modified favouring direct reaction of alkyl radicals with the stabilizers [reactions (7) and (9)].

We plan to undertake time-resolved measurements on solid-state polymers, where the kinetics are more complex and mobility and diffusion data are lacking.

Conclusion

Pulse radiolysis experiments with solutions of DBC and DPA in long-chain n-alkanes yielded information of the type of reaction and reactivity of transient species generated in such systems. It was found that alkyl radicals formed from the solvent react selectively with the labile O-H and N-H bonds of the stabilizers. In contrast, H radicals react with these bonds as well as with the aromatic ring. In case of DPA the radiation-generated triplet decays by H-abstraction from the solvent, forming cyclohexadienyl-type radicals only. Under the described experimental conditions no reaction of alkyl-peroxy radicals could be observed.

The experimental data and the reaction mechanisms given in tables 1-3 give evidence for the interpretation of the stabilization effect under radiation-chemical conditions as being caused preferably by direct reaction of alkyl and hydrogen radicals as primary species according to reactions (7), (9) *etc.* In comparison, the reaction of alkylperoxyradicals [reactions (8) and (10)] plays a minor role as previously supposed.

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