Reactions of Dibenzoyldiazene. Part 2.† Thermal and Photochemical Decompositions in Benzene Solution

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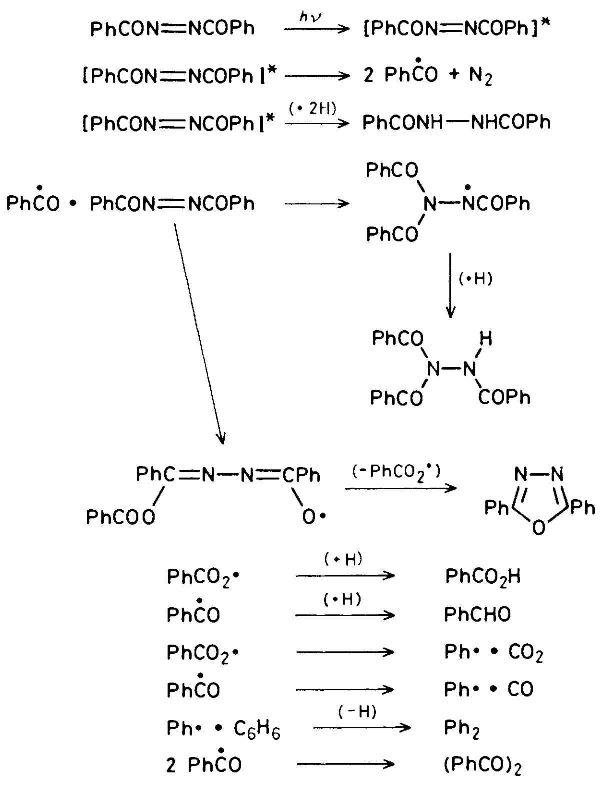
E.s.r. and microsecond flash-photolysis studies indicate that in benzene solution hydrazyl radicals formed by the addition of various precursor radicals to dibenzoyldiazene are deactivated through a second-order process, yielding the corresponding hydrazines. This process occurs in parallel with a pseudo-first-order reaction with dibenzoyldiazene in which an oxygen atom is transferred, yielding the corresponding hydrazoxyl radical and diphenyloxadiazole. A structure–reactivity correlation is noted, and the role played by these reactions in the inhibition and retardation of the radical polymerization of vinyl monomers is discussed.

The complexities of the course of the reaction of radicals with dibenzoyldiazene (DBDZ) were revealed in the mid nineteen-sixties by studies attempting to elucidate the reactions of the free benzoyl radical.[1,2] Quantitative analyses of the products of both thermal and photochemical decompositions of DBDZ in a variety of solvents established yields of di- and tribenzoylhydrazines, diphenyloxadiazole, benzaldehyde, benzoic acid, benzil, and biphenyl along with the gaseous products carbon monoxide, carbon dioxide, and nitrogen. Even when the parent compound was only present at low concentration the yields of tribenzoylhydrazine (TBH) and diphenyloxadiazole (DPO) were significant and were taken to indicate a high radical reactivity with DBDZ at both the azo group and the carbonyl oxygen atom (Scheme 1).

One of the less attractive features of this scheme is the requirement of almost identical radical reactivities at different sites in close proximity within the same substrate. Of greater detraction is a calculable 35% shortfall in the mass balance on the carboxy products that would be predicted to arise from the eliminated benzoyloxyl radical. In the photochemical studies, the decomposition of 100 moles of DBDZ yielded 22 moles of DPO but only 8 moles of benzoic acid and 6 moles of carbon dioxide. The ready formation of hydrazyl radicals, however, was indicated by a 13% yield of TBH and has subsequently been demonstrated by e.s.r. studies.[3] In other carboxydiazene systems, hydrazoxyl radicals have been observed under similar conditions,[4] though the mechanism of their formation in the absence of an oxidant has likewise remained an enigma.

In this paper we (i) report evidence that the formation of the oxadiazole is concomitant with that of a hydrazoxyl radical, and (ii) discuss the reactivity of hydrazyl radicals derived from DBDZ.



Scheme 1.

Experimental

Materials.—The purification of the monomers and solvents and the preparation of azodibenzoyl have been described previously.[5]

Tribenzoylhydrazine was prepared by refluxing equimolar amounts of sodium dibenzoylhydrazinide and benzoyl chloride in dry ether for 3 h. After filtration and extraction of the residue with hot ethanol, white crystals of the product were obtained on cooling; m.p. 575—576 K (lit.,[2] 575—577 K) (Found: C, 73.25, H, 4.6; N, 8.1. Calc. for $C_{21}H_{16}N_2O_3$; C, 73.3; H, 4.65; N, 8.1%).

The other materials used as standards for h.p.l.c. analyses (benzoic acid, benzaldehyde, benzophenone, benzil, biphenyl, and diphenyloxadiazole) were of SLR grade and used without further purification.

Apparatus.—Product analyses by h.p.l.c. were accomplished using a μPorasil column and either benzene or chloroform as the mobile phase.

E.s.r. spectra were obtained using a JEOL JES-PE spectrometer and flash photolyses were carried out on a K-5 flash kinetic spectrophotometer supplied by Applied Photophysics. Steady-state photolyses were carried out using a Hanovia 100 W mercury compact source.

All other apparatus and procedures are described in Part 1.[5]

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† Part 1, ref. 5.

Results and Discussion

Table 1 lists the yields of the organic products resulting from the steady-state photolysis of DBDZ at 0.01 mol dm^{-3} in benzene solution at two temperatures.

The first four of these products are readily identified as the ultimate products of the reactions of primary benzoyl radicals either with themselves or with the solvent, or else of an excited state of DBDZ with the solvent. Of most relevance to the ensuing arguments, however, are the variations in yield of the last three products as the temperature is raised. Even assuming that one of the phenyl groups of the biphenyl arises from the decarbonylation of the primary benzoyl radicals, it appears that the lower yield of TBH at the higher temperature is not only consequent upon this effect, but is fully accommodated only through the increased yield of DPO. Furthermore, the reduced yield of benzaldehyde and the appearance of a yield of benzoic acid in close correspondence at the higher temperature seems to indicate that the latter is an oxidation product of the former rather than the product of a hydrogen-abstraction reaction by a benzoyloxyl radical. An alternative course for the reactions of benzoyl radicals with DBDZ that would rationalize these observations is depicted in Scheme 2, though it must be acknowledged that this goes no further towards explaining the apparent imbalance of the DPO yield and those of the carboxy products.

Figure 1 depicts the e.s.r. spectra of the species that are generated on irradiation of a 0.02 mol dm^{-3} solution of DBDZ in benzene at 333 K. The spectrum (a) is that obtained immediately following the onset of irradiation; (b) is only obtained at the third and subsequent scans. At 303 K, a spectrum identical with that of Figure 1(a) is obtained but the subsequent transformation to the spectrum of Figure 1(b) does not occur. None of the signals is persistent on extinction of the light source.

Figure 1(a) is readily identified as the spectrum of a hydrazyl radical,[3] and the 1:1:1 triplet of 1:1:1 triplets of Figure 1(b) is characteristic of a hydrazoxyl radical.[4] Clearly the latter is not formed in sufficiently high steady-state concentration at 303 K as to mask the hydrazyl signal. At 333 K the observation of a virtually uncorrupted hydrazoxyl signal after a short period following the onset of illumination, though not necessarily indicative of a high steady-state concentration, does suggest that its formation is at the expense of the hydrazyl radical through a relatively slow thermal reaction such as that depicted in Scheme 2.

The spectroscopic parameters are listed in Table 2 together

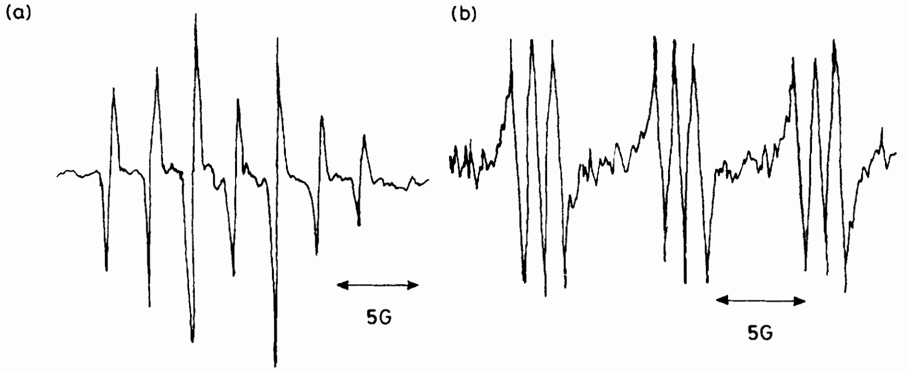


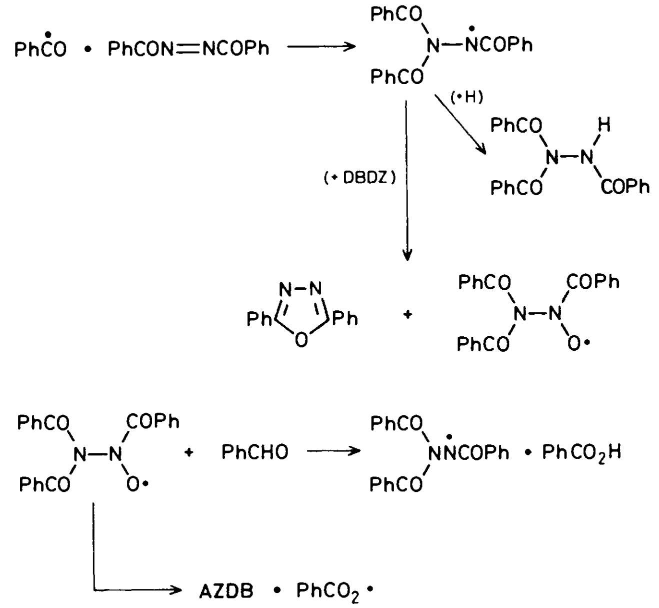
Figure 1. E.s.r. spectra of transients arising from the photolysis of DBDZ (0.02 mol dm^{-3}) in benzene solution at 333 K: (a) first scan, (b) third scan

Table 1. Photodecomposition of dibenzoyldiazene (products per 100 moles of DBDZ reacted)

T/K	Benzaldehyde	Benzil	Benzoic acid	Dibenzoyl-hydrazine	Biphenyl	Tribenzoyl-hydrazine	Diphenyloxa-diazole
303	7	16		1	12	34	15
333	5	16	3	2	20	20	23

Table 2. E.s.r. parameters of transients generated at 333 K

		Hyperfine splittings (G)			
System	*g*	*a*(N-1)	*a*(N-2)	H	Assignment
DBDZ/*h*ν	2.0047	10.3	5.3		Tribenzoylhydrazyl
DBDZ/*h*ν	2.0045	10.1	5.1		Tribenzoylhydrazyl } overlapping
(2nd scan)	2.0060	9.0	1.25		Tribenzoylhydrazoxyl }
DBDZ/*h*ν (3rd scan)	2.0062	8.5	1.5		Tribenzoylhydrazoxyl
DBDZ-AIBN	2.0061	8.4	1.7		Dibenzoyl(cyanoisopropyl)hydrazoxyl
DBDZ-DBP	2.0048	10.2	5.0	?	Hydrazyl } overlapping
(1st scan)	2.0060	7.9	?	?	Hydrazoxyl }
DBDZ-DBP (3rd scan)	2.0063	8.3	1.6	0.8	Hydrazoxyl (weak signal)



Scheme 2.

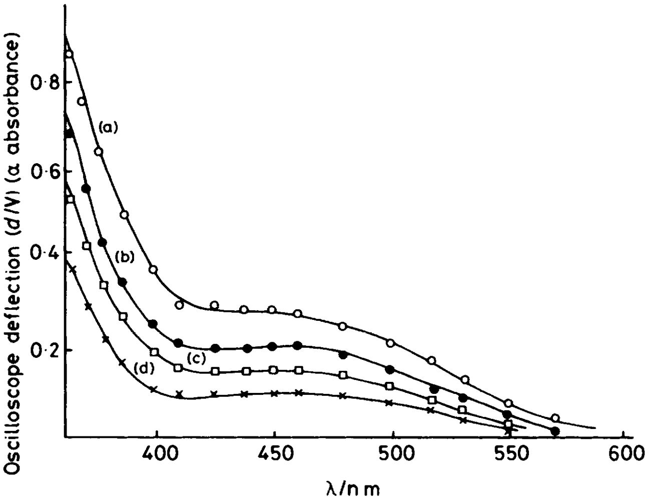


Figure 2. Spectra of the transient observed on flash photolysis of DBDZ (10^{-3} mol dm^{-3}) in benzene solution at 303 K taken at (a) 25 ms, (b) 50 ms), (c) 75 ms, (d) 125 ms after the flash

with those of signals generated under thermal conditions at 333 K through the inclusion of either azobisisobutyronitrile (AIBN) or dibenzoyl peroxide (DBP) at 0.04 mol dm^{-3}. Unless otherwise indicated, the only differences between the first and subsequent scans were in the intensities of the signals.

That a hydrazoxyl radical is readily formed at 333 K in the DBDZ–AIBN system indicates that its generation is not characteristic of reactant species that can only be obtained through photoexcitation. The possibility that benzoyloxyl radicals formed in accordance with Scheme 1 are the precursors of the hydrazoxyl radical generated by photolysis of DBDZ is to be discounted since the hydrazoxyl signal (probably of dibenzoylphenylhydrazoxyl) that eventuates in the DBDZ–DBP thermal stystem is both different from, and far less intense than, that found in the photochemical system.

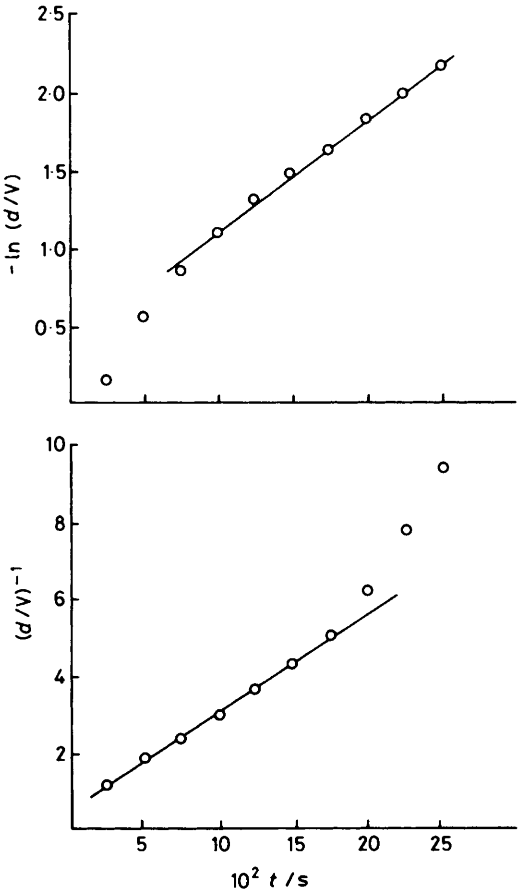


Figure 3. Kinetic plots for the decay of the transient of Figure 2 monitored at 370 nm

Figure 2 shows the decay of the visible absorption spectrum of the transient species observed upon flash photolysis of a 10^{-3} mol dm^{-3} solution of DBDZ in benzene.* The decay is uniform at all wavelengths and as evidenced by the decay plots of Figure 3, a fast second-order reaction gives way to one that is far slower and kinetically first-order. The kinetic parameters from 'first flash' experiments over a range of temperatures are listed in Table 3.

Upon repeated exposure to the flash, during which the DBDZ is progressively consumed, the signal intensity increases up to about the fifth flash, and whilst $k_2/\varepsilon d$ maintains its value, k_1 decreases steadily until the first-order component of decay is no longer evident. Subsequent exposure eventually results in the complete disappearance of the transient.

The transient can be reasonably assigned to the hydrazyl radical by comparison with the spectra and lifetimes of a range of hydrazyls already characterized by flash photolysis.[6] The possibility that it is the hydrazoxyl radical can be discounted since its observation by e.s.r. requires an elevated temperature at which this species is clearly shorter lived. The other possible radicals in the system are known to have either different lifetimes or different spectra. In particular the benzoyloxyl radical displays an absorption maximum at 500 nm and decays by a first-order process with a rate constant of 730 s^{-1} at room temperature.[7]

The initial increase in signal intensity upon repeated exposure

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* The combined effects of a sharp reduction of the spectral intensities from the quartz–iodine monitoring lamp and solvent cut-off result in a rapid deterioration in signal quality at wavelengths less than 370 nm.

Table 3. Kinetic parameters from flash photolyses monitored at 370 nm

		T/K			
		303	313	323	331
Rate constants (s^{-1})	$k_2/\varepsilon d$	110 ± 40	260 ± 50	630 ± 70	1 300 ± 100
	k_1	5.0 ± 1.0	7.2 ± 0.5	10.0 ± 0.5	13.0 ± 0.6

Table 4. E.s.r. parameters of the DBDZ–AIBN–monomer systems in benzene solution at 333 K. [DBDZ] = 0.02 mol dm^{-3}, [AIBN] = 0.04 mol dm^{-3}, [monomer] = 1 mol dm^{-3}

		Hyperfine splittings (G)				
System[a]	*g*	*a*(N-1)	*a*(N-2)	*a*(H)	Signal intensity	Assignment
DBDZ	2.0043	10.0	?		V. weak	Hydrazyl
DBDZ–AIBN–NVC	2.0048	~6	?	?	V. weak	Hydrazyl
DBDZ–AIBN–PMS	2.0040	~7	?	?	V. weak	Hydrazyl
DBDZ–AIBN–STY	2.0043	11.0	6.5	3.0	Strong	Hydrazyl
DBDZ–AIBN–VA	2.0062	8.4	1.7		Weak	Hydrazoxyl
DBDZ–AIBN–MMA	2.0042	11.8	8.8		Strong	Hydrazyl

[a] NVC = *N*-vinylcarbazole, PMS = *p*-methoxystyrene, STY = styrene, VA = vinyl acetate, MMA = methyl methacrylate.

to the flash is attributed to photosensitization of the primary decomposition by benzil formed through the combination of benzoyl radicals produced in the previous flashes. The same effect was observed by including benzil at a concentration of 10^{-4} mol dm^{-3} for the flash photolysis of a fresh solution of DBDZ. The ensuing decrease in the value of the first-order rate constant of decay is indicative of a reaction of the hydrazyl radical with a component of the system with a concentration well in excess of it, but which is progressively being consumed. This is consistent with the reaction that leads to the hydrazoxyl radical and DPO in Scheme 2. The increase in the value of the rate constant with temperature correlates with the Arrhenius equation for an activation energy of 28 kJ mol^{-1} and a frequency factor of 4 × 10^8 dm^3 mol^{-1} s^{-1} at the DBDZ concentration of 10^{-3} mol dm^{-3}; these values are reasonable for a sterically hindered radical–molecule reaction.

The values of $k_2/\varepsilon d$ correlate with the Arrhenius equation for an activation energy of 75 kJ mol^{-1}, which is unusually high even for a radical–radical reaction which is hindered. By analogy with the known ability of diphenylpicrylhydrazyl to abstract hydrogen atoms through a reaction which is second-order with respect to the hydrazyl and which has a comparable activation energy,[8] it is possible that the observed reaction is that which leads to the formation of TBH through the intermediacy of a complex of the radical and the solvent. Evaluation of $A/\varepsilon d$ gives 1.7 × 10^{15} s^{-1}, so since εd is very much greater than unity (ε is probably *ca.* 10^4 dm^3 mol^{-1} cm^{-1} [6] and *d* is 10 cm) it follows that the frequency factor is significantly greater than this value and that the reaction must indeed be complex. This and like reactions are probably worthy of further study, for not only from flash photolysis, but also from product analyses and e.s.r. spectroscopy, it is apparent that tribenzoylhydrazyl must be highly reactive in hydrogen abstraction from benzene.

In an attempt to establish what role, if any, is played by the reactions involving hydrazyl and hydrazoxyl radicals in the inhibition and retardation of radical polymerizations in the presence of DBDZ, e.s.r. spectra of the various DBDZ–monomer systems of Part 1 were obtained under a variety of conditions. The parameters and characterstics of those spectra that proved reproducible are listed in Table 4. Though the available information is therefore limited, it is nonetheless possible to draw some qualitative conclusions about radical stabilities.

With the exception of the vinyl acetate system only signals attributable to hydrazyls were observed. The well defined spectra of the styrene and methyl methacrylate systems are evidently different from any of the previously assigned spectra and it is therefore reasonable to accept that initiation of polymerization has occurred prior to radical addition to DBDZ. From the intensities of the various signals it must be concluded that the stabilities of the hydrazyls of the vinylcarbazole and *p*-methoxystyrene systems are much lower than those of the styrene and methyl methacrylate systems. Since no signals attributable to hydrazoxyls were observed it must be assumed that the deactivation occurs predominantly through the second-order reaction leading to the formation of the corresponding substituted dibenzoylhydrazines. To substantiate this assumption further, e.s.r. spectra were obtained for the corresponding systems under photolysis conditions. A very weak hydrazoxyl signal was eventually discernible for the vinylcarbazole system after about 4 h irradiation, but otherwise only hydrazyl spectra with characteristics similar to those in Table 4 were obtained. Flash photolyses of the same systems confirmed that the second-order rate of deactivation was markedly increased in that for the vinylcarbazole and *p*-methoxystyrene systems no significant transient was observed, whilst in the styrene system additions of the monomer up to a concentration of 0.14 mol dm^{-3} led to a gradual increase to 1 400 s^{-1} in the value of $k_2/\varepsilon d$ at 303 K. The value of k_1 for this system was about 2 s^{-1} and was unaffected by the changing monomer concentration. With such an increased reactivity of the hydrazyls in the monomer-containing systems, that any of them display defined e.s.r. signals must be attributed to an efficient primary radical capture by the monomers such that a higher rate of hydrazyl formation obtains than that in the simple AIBN–DBDZ system. The results further concur with the conclusions of Part 1 in that the weakest e.s.r. signals arise in the systems with the lowest efficiencies of initiation of polymerization.

Vinyl acetate appears to be exceptional in its behaviour in that only the spectrum of a hydrazoxyl radical is observed. Furthermore, the spectrum has parameters very similar to those of the simple AIBN–DBDZ system under the same conditions. However, the corresponding DBDZ–vinyl acetate system under phtolysis conditions behaves differently from the simple DBDZ system under the same conditions. At 333 K only the spectrum of a hydrazoxyl species is observed at the onset of illumination and the temperature has to be reduced to 303 K in order to

Table 5. E.s.r. parameter of the DBDZ–VA/$h\nu$ system in benzene solution. [DBDZ] = 0.02 mol dm^{-3}, [VA] = 1 mol dm^{-3}

		Hyperfine splittings (G)				
T/K	*g*	*a*(N-1)	*a*(N-2)	*a*(H)	Signal intensity	Assignment
333	2.0066	9.0	1.5		Strong	Hydrazoxyl
303 (1st scan)	2.0050	9.0	5.0	1.5	Strong	Hydrazyl
303 (after 80 min)	2.0066	9.0	1.5		Strong	Hydrazoxyl

observe the spectrum of the hydrazyl species from which it is derived. For the purposes of comparison, the e.s.r. parameters of these signals are shown in Table 5. It is apparent that at least in the case of the 'photo' systems, the hydrazoxyl obtained when the monomer is present is different from that obtained in its absence and that the transformation from hydrazyl to hydrazoxyl radical is much more efficient in the system that contains vinyl acetate than in any of the other systems.

In Part 1 we noted the correlation of the reactivities of the monomers with respect to cycloaddition to DBDZ, with the parameters *e* of the *Q*/*e* scheme of Alfrey and Price for rationalizing copolymerization reactivity ratios. The more negative the *e* value, the faster the cycloaddition. Although the foregoing results are for the most part qualitative, it appears nonetheless that a parallel correlation obtains for the reactivities of the various hydrazyl species, *i.e.* the more negative the *e* value of the monomer from which the hydrazyl is derived, the more reactive it is with respect to deactivation by the 'second-order' mechanism, and the lesser its reactivity with DBDZ to form the corresponding hydrazoxyl radical.

In conclusion, it should be noted that the anomalously high rate of consumption of DBDZ through radical pathways in the polymerizing systems can be rationalized by the formation of hydrazoxyl radicals in accordance with Scheme 2.

If we represent hydrazyl radicals, hydrazoxyl radicals, and propagating polymer chain radicals by Hy$^{\cdot}$, HyO$^{\cdot}$, and M$^{\cdot}$, respectively, then the overall reaction course can be summarized as in Scheme 3. Under steady-state conditions equation (i) obtains. If the steady-state radical concentration is low such

Hydrazyl formation $\quad \mathrm{M^{\cdot} + DBDZ \xrightarrow{k_f} Hy^{\cdot}}$ (1)

Hydrazoxyl formation

$\mathrm{Hy^{\cdot} + DBDZ \xrightarrow{k_1} HyO^{\cdot} + DPO}$ (2)

Chain termination $\quad \mathrm{2\,Hy^{\cdot} \xrightarrow[(+H)]{k_2} 2\,HyH}$ (3)

Scheme 3.

$$k_f\,[\mathrm{M^{\cdot}}][\mathrm{DBDZ}] = k_1\,[\mathrm{Hy^{\cdot}}][\mathrm{DBDZ}] + k_2\,[\mathrm{Hy^{\cdot}}]^2 \quad \text{(i)}$$

that $k_1\,[\mathrm{Hy^{\cdot}}][\mathrm{DBDZ}] \gg k_2\,[\mathrm{Hy^{\cdot}}]^2$, then equation (i) reduces to $k_f\,[\mathrm{M^{\cdot}}][\mathrm{DBDZ}] = k_1\,[\mathrm{Hy^{\cdot}}][\mathrm{DBDZ}]$ and for each radical chain initiated two molecules of DBDZ are subsequently consumed. Furthermore, if it is assumed that in the presence of the monomers the predominant fate of the hydrazoxyl radical is to re-initiate polymerization, then Scheme 3 can be extended with the radical propagating reaction (4). Under steady-state conditions equation (ii) now follows, where *k* is the rate constant for the deactivation of the hydrazoxyl radical in the absence of monomer. Not only is there the potential for the consumption of further molecules of DBDZ through what are effectively short chain copolymerizations with the monomers, but it can also be recognized that if $k_1/(k + k_i\,[\mathrm{M}])$ is small, then the observation of the hydrazoxyl radical by e.s.r. would be unlikely even when the steady state is well established. It might thus be concluded that it is only for the DBDZ and the DBDZ–vinyl acetate systems that this condition does not obtain.

$$\mathrm{HyO^{\cdot} + M \longrightarrow M^{\cdot}} \quad (4)$$

$$[\mathrm{HyO^{\cdot}}]/[\mathrm{Hy^{\cdot}}] = k_1\,[\mathrm{DBDZ}]/(k + k_i\,[\mathrm{M}]) \quad \text{(ii)}$$

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