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DPPH (2,2-Diphenyl-1-picrylhydrazyl) as a Diagnostic Tool in Mechanistic Studies Related to Polymerization

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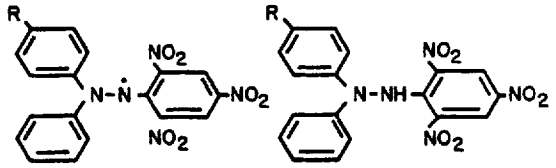
ABSTRACT

The reactions of DPPH with azobisisobutyronitrile in benzene and in methyl methacrylate have been studied. The reactions are complex, and the previously-assumed initiator radical-DPPH adduct, 1-(4-cyanoisopropylphenyl)-1-phenyl-2-picrylhydrazine, is only one component in a mixture of products which include diphenyl, diphenylamine, 1,1-diphenyl-2-picrylhydrazine and aminophenylphenylpicrylhydrazine derivatives, and nitrile-rich polymeric species.
The reactions of DPPH with aliphatic mercaptans are also more complex than previously assumed, and although the corresponding aliphatic disulfides are usually the major products, the reactions apparently do not involve free radical intermediates.

INTRODUCTION

2,2-Diphenyl-1-picrylhydrazyl (DPPH; I) has been widely used for diagnosis of radical processes and as a radical scavenger in the

determination of initiation rates of chain polymerization reactions. However, little is known of the products or the over-all stoichiometry of the reactions between DPPH and organic radicals, except that the products appear to be derivatives of 1,1-diphenyl-2-picrylhydrazine (DPPH.H; II) formed by radical substitution on the phenyl groups and not on the hydrazyl nitrogen (Fig. 1).



I R=H-
III R=$(CH_3)_2C(CN)$-

II R=H-
III R=$(CH_3)_2C(CN)$-

FIG. 1

The use of DPPH as a radical scavenger in kinetics studies is based on sometimes-questioned assumptions that DPPH reacts rapidly with equimolar amounts of the organic radical species present in the reaction mixture; that the products of the scavenging reaction are inert, i.e., they themselves are not radical scavengers or retard radical chain reactions; that there is no prior complex formation between the radical precursor and DPPH, or induced decomposition of the precursor by DPPH or its products; that DPPH itself does not initiate chain reactions.

Although there is little evidence for the initiation of polymerization by DPPH, adduct formation and induced decomposition have been observed in systems containing peroxides, hydroperoxides, peresters, or species with active or acidic hydrogen atoms. DPPH also undergoes rapid decomposition when irradiated with visible or uv light.

The scavenged reaction products, consisting of nitroaromatic compounds with oxidizable amine or hydrazine functional groups, are not truly inert towards radical processes. DPPH.H, for example, is almost as effective an inhibitor for the polymerization of some monomers as DPPH itself, and it is readily oxidized to DPPH by such species as the cyanoisopropyl radicals (CPR) produced by the decomposition of azobisisobutyronitrile (ABIB) [1, 2].

The stoichiometry and efficiency of the radical scavenging reactions of DPPH have been questioned by many workers who have reported apparent efficiencies significantly greater or less than 100%. We therefore chose to investigate one particular system in detail, the reaction between DPPH and thermally-generated CPR.

RESULTS AND DISCUSSION

The decomposition of ABIB has been extensively studied by Hammond and co-workers [3] and others, who have postulated the reaction sequence of Fig. 2.

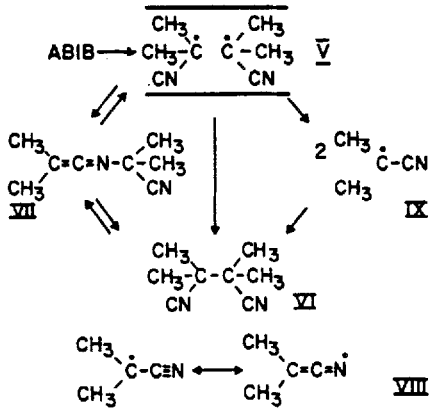


FIG. 2.

The geminate CPR (V) may recombine within their solvent cage to yield tetramethylsuccinodinitrile (TMSN; VI), or the unstable isomeric ketenimine (VII) via the mesomeric radical species (VIII). Alternatively, the CPR diffuse from the solvent cage and are free to react with other components of the reacting system. In the presence of reactive monomers or radical scavengers, about 70% of the original geminate CPR, namely the free CPR fraction (IX) can be trapped or utilized in chain initiation reactions [4].

We found that the products of the reaction between theoretically-equivalent amounts of DPPH (2.00 moles) and ABIB (1.00 mole) in benzene at 60°C included diphenyl (0.01 mole), diphenylamine (0.02 mole), TMSN (0.16 mole), DPPH.H (trace), DPPH (0.56 mole), 1-(4-cyanoisopropylphenyl)-1-phenyl-2-picrylhydrazine (IV; 0.84 mole), putative bis(cyanoisopropylphenyl)picrylhydrazine (trace), and a nitrile-rich polymeric residue. No isobutyronitrile or methacrylonitrile were detected in the products, indicating the absence of disproportionation between CPR. The total hydrazyl radical content of the products was equivalent to 0.66 mole of DPPH.

The 1-(4-cyanoisopropylphenyl)-1-phenyl-2-picrylhydrazine was identified by means of ir and mass spectroscopy. Like DPPH.H, it was readily oxidized by lead dioxide to the corresponding stable hydrazyl (III) which had visible and ESR spectra similar to those of DPPH. The polymeric residue, on the basis of its ir spectrum, appears to contain a large proportion of CPR-derived aliphatic nitrile components. The nature of these has not been determined, although mass spectral evidence indicates the presence of amino-substituted DPPH derivatives, presumably formed from the dimethylketenimino radical-DPPH adduct by CPR attack and/or decomposition during subsequent work-up. The absence of methacrylonitrile in the products and the persistance of added trace amounts of this monomer in reacting DPPH-ABIB mixtures support this hypothesis. There is obviously reoxidation of DPPH.H and its derivatives during the reaction, but the nature of the oxidant is uncertain. Both DPPH and DPPH.H are stable under the conditions used for the DPPH-ABIB reaction.

The effective stoichiometry of the scavenging reaction in benzene, after correction for the proportion of CPR utilized in TMSN formation, corresponds to ~80% scavenging efficiency:

1.00 ABIB – 1.68 free CPR
1.68 free CPR + 1.34 DPPH – "inert" products

The efficiency of DPPH in scavenging potential chain initiators is thus lower than often assumed, and DPPH may not completely inhibit polymerization of monomers present in high concentration in the reaction mixtures. The complexity of the reaction is illustrated by the observation that only ~50% of the scavenged CPR can be recovered as a simple derivative.

In previous studies of the reaction of DPPH with hydroperoxides, and with adsorbed water or surface hydroxyl groups on mineral fillers [5], we found that the oxidation by DPPH probably proceeds by an ionic rather than by a purely radical process. The products appeared to be formed via a semidine-like rearrangement of the putative N-hydroxy-diphenylpicrylhydrazine.

Nonradical dehydrogenation reactions have also been postulated by Matevosyan and co-workers [6], who suggest that DPPH coexists with its charge-transfer dimer, the actual active species:

$$2\mathrm{DPPH}^{\cdot} \rightleftharpoons [\mathrm{DPPH}^{+}.\mathrm{DPPH}^{-}] \xrightarrow{XH} \mathrm{DPPH}^{\cdot} + \dot{X} + \mathrm{DPPH.H};\ \text{etc.}$$

These reactions have considerable significance as the disappearance of the characteristic color or ESR spectrum of DPPH is often

used as diagnostic evidence for radical reaction mechanisms or intermediates.

The dehydrogenation of aliphatic mercaptans by DPPH was therefore re-examined for possible nonradical reaction mechanisms. Preliminary results are reported here; the complete results will be published at a later date.

Previous workers [7-9] had found that the kinetics of the reaction, in the presence of a large excess of mercaptan, were first order with respect to both mercaptan and DPPH, and the following mechanism was postulated:

$$RSH + DPPH^{\cdot} - RS + DPPH.H$$

$$2RS^{\cdot} - RSSR$$

$$RS^{\cdot} + DPPH^{\cdot} - RS.DPPH$$

However, the products of the reactions had not been identified, apart from DPPH.H fractions which were tenaciously contaminated with a sulfur-containing species presumed to be the thiyl radical-DPPH adduct.

We found that the reactions yielded dialkyl disulfides as previously supposed, but that the percentage conversion of the mercaptan to disulfide was markedly dependent on steric factors as well as the ratio of the reagents (Table 1).

TABLE 1. Percentage Conversion of Mercaptan to Disulfide

(a) Ratio DPPH/RSH, 1:1	
Primary mercaptan	~75%
Hindered primary mercaptan	~40%
Secondary mercaptan	~40%
Tertiary mercaptan	~ 6%
(b) Ethyl mercaptan and DPPH	
2 EtSH:1 DPPH	85%
1 EtSH:1 DPPH	78%
0.6 EtSH:1 DPPH	65%
0.4 EtSH:1 DPPH	32%
0.2 EtSH:1 DPPH	24%

In contrast, the various disulfides could be prepared in almost quantitative yields by conventional free-radical oxidation of the respective mercaptans.

Other products of the reactions included residual mercaptan (even in the presence of excess DPPH), diphenylamine, picramide (or a hydrolyzable precursor), DPPH.H, putative 1-(4-alkylmercapto-phenyl)-1-phenyl-2-picrylhydrazines (RS.DPPH), and a sulfur-rich polymeric residue. The RS.DPPH species could not be separated from the DPPH.H fraction, although they could be identified in the mass spectra of the latter; they appeared to be only minor products, even when excess DPPH reagent was used.

When methyl methacrylate or styrene was used as solvent no polymerization was observed, and no thiyl radical-solvent utilization of these monomers when they were used in low concentrations in benzene solutions. Only traces of solvent-derived species were apparent in the ir spectra of the sulfur-containing polymeric residues. As the rate of dimerization of thiyl radicals is slower than the rate of attack on these monomers, the apparent absence of thiyl radical-solvent derived products indicates that, if radical intermediates are formed in the reaction, they cannot be regarded as being "free."

The kinetics of the mercaptan-DPPH reactions were found to be more complex than previously reported. The reaction between DPPH and an equimolar amount of ethyl mercaptan in benzene followed second-order kinetics over the range of 15-80% reaction of DPPH, in agreement with earlier published results. However, when a twofold excess of DPPH was used, the reaction still followed second-order kinetics, over the initial stages at least, but diethyl disulfide production virtually ceased after ~40% reaction of the mercaptan. This indicates that the reaction proceeds via one or more intermediates with alternative modes of reaction or decomposition.

We propose (Fig. 3) that the initial rate-determining step involves the formation of a transient DPPH.H-thiyl radical adduct (X), which, however, could not be detected in the ESR spectrum of reacting ethyl mercaptan-DPPH mixture. (A transient radical species is detected in the thiophenol-DPPH reaction.) These complexes would be relatively inert; trinitrobenzene, for example, is known to suppress the peroxide-catalyzed addition of thiols to alkenes. In the present reactions, disulfide formation appears to proceed through a second intermediate which, we propose, is formed by a rapid reaction between the adduct X and DPPH, yielding either the alkylmercapto derivative (RS.DPPH; XII) or the sulfenamide (XI). It is known that the sulfenamides, particularly acyl-sulfenamides or acyl-sulfenhydrazides, react with mercaptans to yield disulfides, and the picryl-sulfen-hydrazides would be expected to undergo similar reactions. The alkyl sulfenamides also readily decompose, yielding amine plus putative unstable thiocarbonyl species which rapidly polymerize. The intermediate XI could similarly decompose yielding DPPH.H and sulfur-rich polymer, and this reaction would

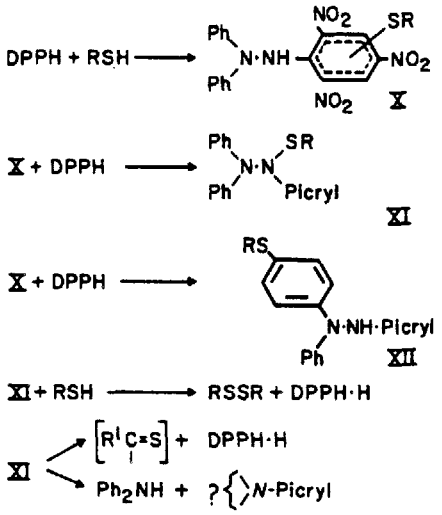


FIG. 3

be more prominent when excess DPPH was present in the mixture, or when steric factors limit the ease of reaction between the intermediate XI and, for example, neopentyl or tert-butyl mercaptans. The diphenylamine and picramide found in the reaction products presumably arise by an alternative mode of decomposition of XI involving N—N fission. In passing, there was no apparent reaction between the mercaptans and DPPH.H, or between the disulfides and DPPH under the conditions used in the DPPH-mercaptan reactions.

EXPERIMENTAL

DPPH was purified by recrystallization from benzene-petroleum ether, followed by drying at 80°C/0.05 mm for 16 hr to remove solvent of crystallization. ABIB was recrystallized from methanol, and the other reagents were purified using conventional procedures. The reactions of DPPH were conducted in rigorously outgassed solutions in the absence of light.

DPPH and ABIB in Benzene

The solution containing DPPH (5.6 mM) and ABIB (2.8 mM) was heated at 60°C for 72 hr to ensure virtually complete decomposition

of the initiator. A portion of the product was assayed for TMSN and other volatiles by means of gas chromatography, and for total hydrazyl content by ESR and visible spectroscopy. The remainder was fractionated by quantitative chromatography on silica, and the fractions examined using ir and mass spectroscopy. The 1-(4-cyanoisopropylphenyl)-1-phenyl-2-picrylhydrazine fraction was recrystallized from benzene as orange needles, mp 154°C; ir spectroscopic comparison with DPPH.H indicated absorption at 840 cm^{-1} due to p-phenyl substituents, and at 2250 cm^{-1} due to nitrile. The mass spectrum of the adduct was anomalous in that both the parent ion (m/e 462) and cyanoisopropyldiphenylamino fragment (m/e 236) eliminated CH_3 instead of the expected HCN; 1-methyl-1-phenylpropionitrile showed similar fragmentation behavior.

The reaction of DPPH with ABIB was repeated using chlorobenzene as solvent to check for volatile products having GLC retention volumes similar to that of benzene. The reaction in methyl methacrylate was performed using an equal volume of benzene as diluent; the subsequent work-up procedure was similar to that outlined above.

DPPH and Aliphatic Mercaptans

In a typical reaction, using ethyl mercaptan, equimolar amounts of DPPH and mercaptan (10 mM) in benzene were reacted at 20°C for 24 hr. The solvent and volatile products were removed using high-vacuum evaporation at 30°C, and the recovered volatiles examined by gas chromatography. The diethyl disulfide was isolated using preparative GLC and identified by mass spectroscopy. Solutions of the nonvolatile residue were also examined using GLC and then fractionated using column and preparative thin-layer chromatography on silica. The fractions were examined by ir and mass spectroscopy. The mass spectrum of the DPPH.H fraction only indirectly showed the presence of 1-(4-ethylmercaptophenyl)-1-phenyl-2-picrylhydrazine by the appearance of an ion m/e 200 due to a thiodiphenylamino fragment; the parent ion was not visible, and the expected ethylmercaptodiphenylamino fragment was masked by ions due to the picramide moiety. Reductive fission of the DPPH.H fraction yielded a mixture of diphenylamine and 4-ethylmercaptodiphenylamine, and the latter was identified by comparison with an authentic specimen.

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