

Heptyl 2-Cyanopropan-2-yl Peroxides from the AIBN-initiated Autoxidation of Heptane

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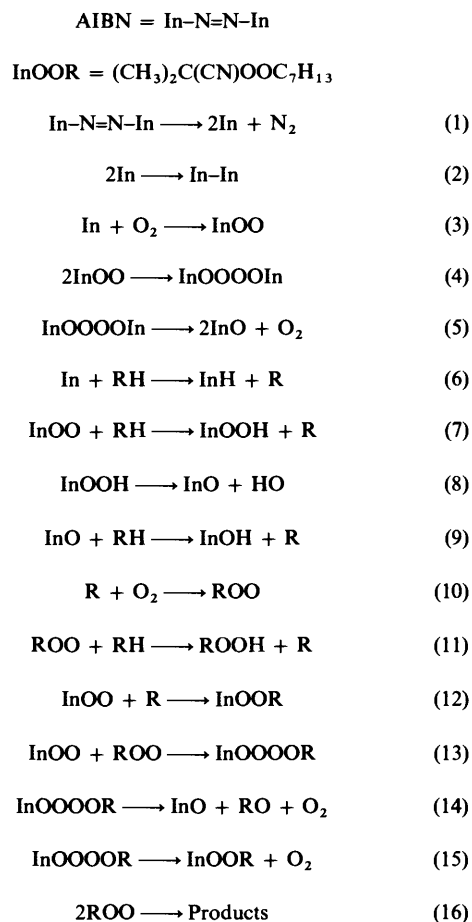
The role of AIBN in the autoxidation of hydrocarbons and the reactivity of the 2-cyanopropan-2-yl peroxy radical is discussed.

The recent reports^{1,2} that unsymmetrical dialkyl peroxides were produced in the dioxygen oxidation of γ -tocopherol which was initiated by 2,2'-azobis(2,4-dimethylvaleronitrile) prompts us to report a similar product obtained in the azoisobutyronitrile (AIBN) initiated autoxidation of heptane.

Hammond and co-workers³ have made an extensive study on the mechanism of decomposition of 2,2'-azoalkylnitriles and they and Walling⁴ demonstrated that these compounds are inefficient in producing radicals owing to cage and non-cage dimerisations. However, AIBN and related compounds have enjoyed considerable attention⁵ as initiators for, amongst other reactions, autoxidation studies and these investigations have led to a fundamental understanding of free radical processes. In kinetic studies of autoxidation reactions the rate constants for the reaction of peroxy radicals has been obtained from the initial period of the reaction with constant initiation. The results of this report show that mixed peroxides are formed by reaction between the initiator and substrate radicals. Hence this is another pathway for oxygen consumption and also demonstrates the participation of the initiator radicals in a termination reaction. 2-Cyanopropan-2-yl radicals have also been added to cyclooctatetraene⁶ and benzoquinone⁷ and abstracted hydrogen from good hydrogen donors.⁷

During the course of our product studies of the AIBN-initiated autoxidation of heptane at 100 °C, it was found that with small amounts of initiator the reaction terminated after a short period and that the total molar amount of ketones and alcohols formed was significantly less than the amount of AIBN used as initiator. In addition capillary GLC analysis showed the presence of other compounds with longer retention times than the ketones and alcohols. Since it was suspected that these could be mixed dimeric species produced by reaction of substrate and 2-cyanopropyl radicals, the reaction of heptane and AIBN was carried out in the absence of oxygen. This reaction mixture produced 2,3-dicyano-2,3-dimethylbutane as the only significant product [Scheme 1, eqn. (2)]. In the presence of oxygen the reaction of heptane with increasing amounts of AIBN produced increased yields of the additional compounds with longer retention times than the ketones and alcohols. Two of the five compounds with longer retention times were identified as 2,3-dicyano-2,3-dimethylbutane (In-In) and acetone cyanhydrin (InOH) respectively.

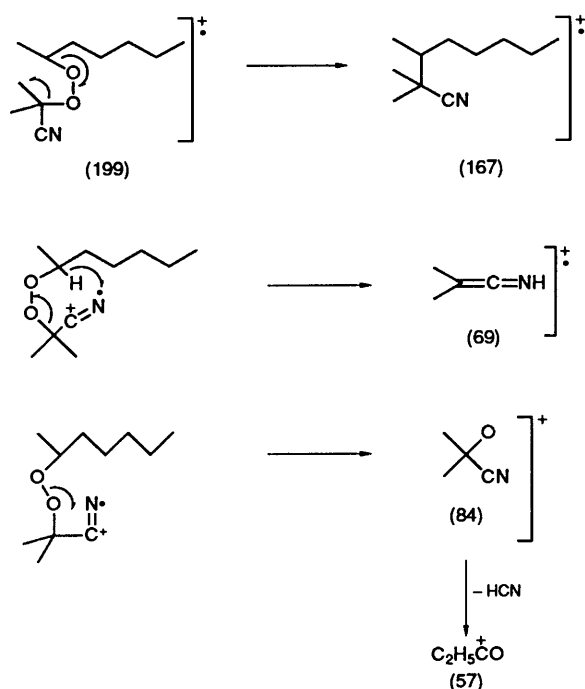
In order to identify the other three compounds with close retention times in the capillary GLC analysis, the reaction mixture was separated by repeated TLC chromatography which afforded a fraction which was shown by capillary GLC analysis to be a mixture of the three unidentified components which had very similar retention times. This mixture of compounds was concluded to be an isomeric mixture of heptan-2-, 3- and 4-yl 2-cyanopropan-2-yl peroxides (InOOR) from elemental and spectral analysis. Capillary GC-MS analysis of each of the three components were almost identical. The mass



Scheme 1

spectra of two of the components showed a small molecular ion at $m/z = 199$ and all three had prominent peaks at $m/z = 167, 84, 69$ (100%), 57, 43 and 41. A suggested fragmentation for one isomer is outlined in Scheme 2. These major peaks are attributed to ions produced by oxygen extrusion from the mixed peroxides, 2-cyano-2-oxypropane, protonated dimethyl ketene and ethyl carbonyl respectively. The NMR spectrum of the mixture had low field multiplets at 4.24 and 4.12, attributed to the proton on carbons which contain the peroxy substituent, further supports the structural assignment.

With large amounts of AIBN in reactions to promote mixed peroxide formation, the amount of acetone cyanhydrin (InOH) exceeded the amount of 2-cyanopropan-2-yl hydroperoxide (InOOH) produced in the reaction mixture. This was established by capillary GLC analysis of the reaction mixture prior



Scheme 1 Fragmentation of heptan-yl 2-cyanopropan-2-yl peroxide

to and after treatment of an aliquot with triphenylphosphine. Since triphenylphosphine is an established reagent⁸ for the reduction of hydroperoxides to alcohols, the increase in acetone cyanhydrin concentration after triphenylphosphine reduction is due to 2-cyanopropan-2-yl hydroperoxide. The formation of the cyanhydrin in excess of its hydroperoxy derivative indicates that the 2-cyanopropan-2-yloxy radical (InO) is the major species which abstracts hydrogen from heptane [eqn. (9)]. The low yield of 2-cyanopropan-2-yl hydroperoxide (InOOH) thus indicates that hydrogen abstraction from heptane by 2-cyanopropan-2-ylperoxy radicals [eqn. (7)] is either not a major process or that the 2-cyanopropan-2-yl hydroperoxide (InOOH) is unstable under the reaction conditions [eqn. (8)]. Since less heptanones and heptanols are produced than the amount of initiator added and that the reaction terminates after 3 h, it is concluded that the AIBN-initiated autoxidation reaction of heptane at 100 °C has very short radical chains, *i.e.* eqn. (11) is a minor process. This implies that the heptyl radicals (R) produced either react with oxygen to produce heptyl peroxy radicals [eqn. (10)] which undergo termination reactions or they are trapped with 2-cyanopropan-2-ylperoxy radicals to generate the mixed peroxide [eqn. (12)].

In reactions with large amounts of initiator added to promote mixed peroxide (InOOR) formation, it was found that the yield of mixed peroxides relative to oxidation products decreased with time. This suggests that mixed peroxide formation occurs more readily in the initial stages of the reaction, whereas the formation of alcohols and ketones occurs by an autoxidative process which is promoted by decomposition of peroxidic material. In confirmation of this it was demonstrated by titrimetric analysis of an aliquot at the end of the reaction that hydroperoxides are produced during the autoxidation process. When air was used in the AIBN-initiated autoxidation, the yields of the mixed peroxides relative to oxidation products increased when the GLC peak areas of the products were compared with those obtained when oxygen was used. Thus at lower oxygen concentrations termination by the formation of mixed peroxides occurs more readily than propagation. This indicates that mixed peroxide formation by condensation of the

2-cyanopropan-2-ylperoxy radical with the alkyl radical [eqn. (12)] is more important than oxygen extrusion from the tetroxide [eqn. (15)].

Further, these peroxy radicals (InOO) are present in reasonable concentration since they either compete [eqn. (12)] with oxygen trapping of the alkyl radicals [eqn. (10)] produced in a propagating step, or react with the alkyl peroxy radicals [eqn. (13)] in competition with hydrogen abstraction by the alkyl peroxy radicals [eqn. (11)] to form a tetroxide⁹ [eqn. (13)]. The mixed tetroxide could subsequently decompose to produce the mixed peroxide [eqn. (15)] in preference to chain propagation [eqn. (14)].

These results confirm the inefficiency of AIBN as an initiator in autoxidation reactions and presents evidence that the 2-cyanopropan-2-ylperoxy radical (InOO) is relatively unreactive since it participates as a radical trap.

Experimental

AIBN-initiated Autoxidation of Heptane.—Heptane (49 cm³) and nitrobenzene (0 or 1 cm³) were heated under reflux with a stream of oxygen or air bubbling through the reaction mixture. AIBN (0.23–5.23 g) was added either in one batch or portionwise over a period of 5 h. Aliquots were removed at regular intervals and analysed (GLC) on a capillary column (Supelcowax TM 10), N₂ (0.61 cm³ min⁻¹), *T* (50 °C for 3 min and then increasing at 10 °C min⁻¹ to 220 °C which was held for 4 min). GC-MS as well as comparison with authentic samples identified the products as heptan-4-one (2.68 min), heptan-3-one (3.09 min), heptan-2-one (5.24 min), heptan-4-ol (5.24 min), heptan-3-ol (5.42 min), heptan-2-ol (5.84 min), the mixed heptyl 2-cyanopropan-2-yl peroxides (9.02–9.65 min), tetramethylsuccinonitrile (10.28 min) and acetone cyanhydrin (10.68 min). The mixed heptyl 2-cyanopropan-2-yl peroxides were isolated by successive TLC separations, δ_{H} (200 MHz) 4.28 and 4.12 (q and m, 1 H), 1.75–1.2 (m, 18 H) and 1.0–0.8 (m, 5 H) (Found: C, 66.3; H, 10.5; N, 6.9. Calc. for C₁₁H₂₁NO₂: C, 66.33; H, 10.55; N, 7.04%).

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