2-(t-Butylazo)prop-2-yl Hydroperoxide: A Convenient Source of Hydroxyl Radicals in Organic Media

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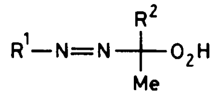
In the presence of a suitable nitroxide, 2-(t-butylazo)prop-2-yl hydroperoxide (**1a**) decomposes cleanly into hydroxyl and t-butyl radicals; the rate constant for its disappearance in cyclohexane is given by: $k = 9.58 \times 10^{14}\ \exp.(-1.47 \times 10^{4}/T)\mathrm{s}^{-1}$.

In order to pursue our investigations into the reactions of free radicals with polymerizable alkenes,[1] we required a clean, thermal source of hydroxyl radicals in organic solution. In this communication we describe the use of 2-(t-butylazo)prop-2-yl hydroperoxide (**1a**), in conjunction with a nitroxide as a free-radical trap,[2] to study the reactions of hydroxyl radicals with organic substrates. The role of the nitroxide in this reaction is to scavenge t-butyl radicals generated from (**1a**), as well as to trap the radicals produced from the reactions of hydroxyl radicals with the substrate.†

Azohydroperoxide (**1a**) has been shown to initiate free radical polymerization of several alkenes.[5] It can be readily prepared by oxygenation of acetone t-butylhydrazone,[6] and is a colourless oil which is stable for several months at −20 °C.

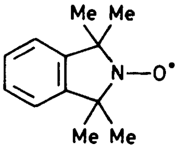
When a degassed solution of (**1a**) (0.034 M) and nitroxide (**2**) (0.14 M) in cyclohexane (10.0 ml) was heated at 70 °C for 17 h, the major products were acetone (100%), 2-methylpropene (15%), and the two adducts (**3**)‡ and (**4**)[1] (82% and 96% respectively). The formation of these products is outlined in Scheme 1. Thus thermolysis of azohydroperoxide (**1a**) generates t-butyl and hydroxyl radicals, as well as acetone and nitrogen. t-Butyl radicals can either couple with nitroxide (**2**) to form adduct (**3**), or donate a hydrogen atom to another radical species present in the mixture to produce 2-methylpropene. Hydroxyl radicals abstract hydrogen atoms from the solvent to give cyclohexyl radicals, which then couple rapidly with nitroxide (**2**) to produce adduct (**4**). (In the presence of high concentrations of a reactive substrate, such as cyclohexane, reaction of hydroxyl radicals with nitroxide is not observed.)



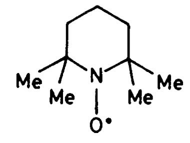
$\mathrm{R^1{-}N{=}N{-}\overset{R^2}{\underset{Me}{C}}{-}O_2H}$

(**1**)

a; $R^1 = Bu^t$, $R^2 = Me$
b; $R^1 = Aryl$, $R^2 = Me$
c; $R^1 = HO_2C(Ph)(Me)$, $R^2 = Ph$



(**2**)



(**5**)

Decomposition of azohydroperoxide (**1a**) (0.1 M) in benzene at 60 °C produced a complex mixture of products. The relatively high yield of t-butyl alcohol (45%) indicates a radical chain mechanism involving induced decomposition of the initiator, equation (1). As was observed in earlier work

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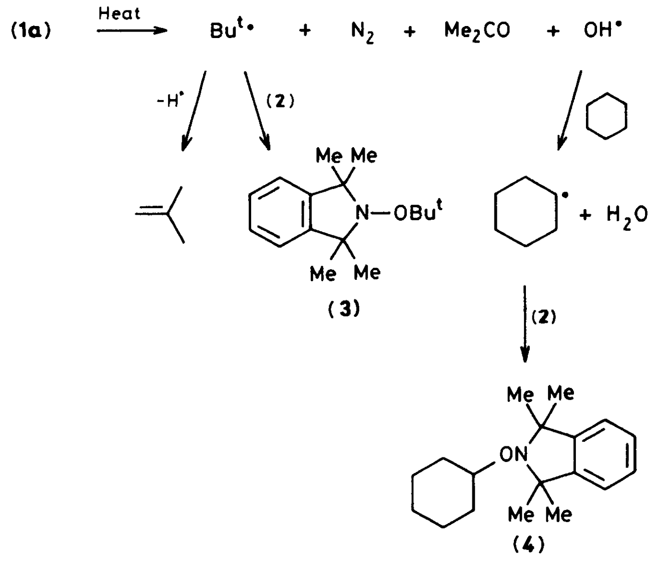
† It is known that α-(arylazo)hydroperoxides (**1b**) produce hydroxyl radicals on thermolysis (ref. 3). However these compounds were considered to be unsuitable for our purposes, since our earlier work suggested that aryl radicals are not efficiently scavenged by nitroxides (ref. 4), and could therefore react with the substrate under the conditions of the present experiment. Bishydroperoxide (**1c**) has the potential of being a particularly clean source of hydroxyl radicals, however our attempts to obtain (**1c**) from the corresponding bischloro compound [1,1′-azobis(1-chloro-1-phenylethane)] were unsuccessful, apparently owing to the instability of the desired product.

‡ Compound (**3**) gave satisfactory spectral and elemental analysis.



Scheme 1

using arylazohydroperoxides (**1b**),[3] the yield of phenol in the present experiment was low (8%). However in the presence of 1.4 equivalents of nitroxide (**2**), the yield of phenol increased to 39%. In this case the nitroxide can act both as an oxidant towards the intermediate hydroxycyclohexadienyl radicals and as an inhibitor of induced decomposition of the initiator.

$$\mathrm{Bu^t\cdot + HO{-}OC(Me)_2{-}N_2{-}Bu^t \rightarrow Bu^tOH + Me_2CO + N_2 + Bu^t\cdot} \quad (1)$$

The kinetics of decomposition of azohydroperoxide (**1a**) were investigated by monitoring its absorption at 368 nm (ε 21 dm^3 mol^{-1} cm^{-1}). Decay of (**1a**) in either cyclohexane or benzene was not first order. However, in the presence of 2 equivalents of nitroxide (**5**) and with cyclohexane as solvent, its decomposition followed first order kinetics, with rate constants 4.86×10^{-4}, 1.24×10^{-4}, 4.29×10^{-5}, and 2.48×10^{-5} s^{-1} at temperatures of 76.5, 65.5, 58.5, and 53.0 °C respectively. [Nitroxide (**5**) was used in experiments on kinetics, since it is essentially transparent at 368 nm.] It was not possible to monitor the decay of (**1a**) in benzene in the presence of a nitroxide, owing to the formation of a species which absorbed at 368 nm.

From the above data, Arrhenius parameters $A = 9.58 \times 10^{14}$ s^{-1} and $E_A = 1.22 \times 10^5$ J mol^{-1}, and activation parameters $\Delta H^\ddagger = 1.20 \times 10^5$ J mol^{-1} and $\Delta S^\ddagger = 33.1$ J K^{-1} mol^{-1} were calculated.

The results presented here demonstrate that the use of azohydroperoxide (**1a**) with a suitable nitroxide can be an effective method for examining the reactions of hydroxyl radicals in organic media. The application of this technique to the investigation of some reactions of hydroxyl radicals with polymerizable alkenes will be published separately.

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References

1 R. D. Grant, P. G. Griffiths, G. Moad, E. Rizzardo, and D. H. Solomon, *Aust. J. Chem.*, 1983, **36**, 2447 and references therein.
2 P. G. Griffiths, E. Rizzardo, and D. H. Solomon, *Tetrahedron Lett.*, 1982, **23**, 1309.
3 T. Tezuka and N. Narita, *J. Am. Chem. Soc.*, 1979, **101**, 7413; T. Tezuka, N. Narita, W. Ando, and S. Oae, *ibid.*, 1981, **103**, 3045.
4 G. Moad, E. Rizzardo, and D. H. Solomon, *Aust. J. Chem.*, 1983, **36**, 1573.
5 R. E. MacLeay and C. S. Sheppard, U.S.P. 4 010 152/1977; Can. P. 964 647/1975.
6 A. S. Nazran and J. Warkentin, *J. Am. Chem. Soc.*, 1982, **104**, 6405.