Oxidative Induced Decomposition of Azobis-α-phenylethane

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Summary Azobis-α-phenylethane decomposes much more rapidly under oxygen than under nitrogen and this oxidative induced decomposition is suppressed by radical scavengers or transition metal ions.

Azo compounds, widely used as initiators in autoxidation and radical polymerization, are accepted to be stable towards free radicals and their induced decomposition has not yet been reported. We report the first evidence of the induced decomposition of azobis-α-phenylethane (APE) and that it can be effectively suppressed by transition metal ions as well as by radical scavengers.

APE decomposes unimolecularly, and under nitrogen or *in vacuo* the decomposition rate constant is independent of both the initial APE concentration and the presence or absence of the radical scavenger, 2,6-di-t-butyl-4-methylphenol (BMP). The rate constant for the decomposition was found to be $1{\cdot}19 \times 10^{-5}\,s^{-1}$ at 90 °C in PhCl and the half life was calculated as 16·2 h. However, APE decomposed rapidly in the presence of oxygen; with sufficient oxygen (Table, run 2) it decomposed completely within 30 min with quantitative evolution of N_2. With insufficient oxygen (Table, run 3), APE decomposed rapidly until the oxygen was exhausted, then the rate of decomposition was the same as that under nitrogen. Introduction of more oxygen brought about resumption of the oxidative induced decomposition.

The addition of BMP decreases the rate of gas absorption by a factor of *ca.* 100 (Table, run 4), which implies that BMP effectively scavenges the α-phenylethylperoxyl radical and suppresses the induced decomposition. The rate of gas absorption in the presence of BMP may be expressed by $(2e - 1)k_d[\mathrm{APE}]$, where k_d is the unimolecular decomposition rate constant and e is the efficiency of radical production which was calculated as 0·81. It is interesting that transition metal salts, such as manganese(II) and cobalt(II) decanoates, are also effective in suppressing the induced decomposition, apparently owing to the trapping of the peroxyl radical by these metal ions. This may be responsible for the inhibiting function of metal salts in autoxidation under certain conditions.[1]

In the absence of oxygen, APE gave nitrogen, 2,3-diphenylbutanes, and traces of ethylbenzene and styrene. Major products in the oxidative induced decomposition of APE were α-phenylethyl hydroperoxide, acetophenone, and methylphenylmethanol with small amounts of PhCHO, $PhCO_2H$, H_2O_2, MeOH, MeOOH, and HCO_2H. Gel permeation chromatographic analysis showed the formation of some products with molecular weights in the order of a few hundred. 2,3-Diphenylbutane and hydrazine derivatives were not detected under oxygen.

A possible mechanism of the induced decomposition is as follows. Since induced decomposition was not observed in the absence of oxygen and α-phenylethyl

TABLE. Decomposition of azobis-α-phenylethane in PhCl (90 °C, 2 h).

Run	APE/mmol	$-d[\mathrm{Gas}]/dt$[a] $\times 10^7/l\ mol^{-1}\ s^{-1}$	Initial O_2/mol	ΔO_2/ mmol	ΔN_2/mmol
1	0·500	−5·93	0		0·0461
2	0·259	514	1·013	0·662	0·252
3	0·500	702	0·749	0·738	0·354
4[b]	0·500	3·61			
5[c]	0·500	6·14	0·615	0·140	0·0978
6[d]	0·501	3·40	0·521	0·124	0·0917

[a] Observed rate of gas absorption. [b] With 0·894 mmol of BMP. [c] With 0·0335 mmol of manganese(II) decanoate. [d] With 0·0288 mmol of cobalt(II) decanoate.

hydroperoxide was the major product (*ca.* 0·8 mol per mol of APE), the primary step in the induced decomposition may be the attack of α-phenylethylperoxyl radical on the tertiary hydrogen atom of APE. The resulting radical would react with oxygen immediately and the peroxyl radical thus formed would cleave to give nitrogen, α-phenylethyl radical, and a biradical (or possibly α-phenyl-α-hydroperoxyethylene), which would undergo further reactions.

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[1] A. T. Betts and N. Uri, *Makromol. Chem.*, 1966, **95**, 22.