Study on Radical Chemistry of Monoperoxycarbonates by α-Methylstyrene Dimer Trapping Technique

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ABSTRACT: The initiation mechanisms of *OO-t*-butyl *O*-isopropyl peroxycarbonate (BuI) and *OO-t*-hexyl *O*-isopropyl peroxycarbonate (HexI) were studied at 140°C by α -methylstyrene dimer (MSD) trapping. Alkoxycarbonyloxy radicals (carbonate radicals) produced from the peroxides were trapped by MSD almost quantitatively, indicating that decarboxylation of carbonate radicals was too slow to compete with addition to the styreneic double bond even at high temperature. The hydrogen abstraction ability of these peroxides was evaluated in a mixture of MSD and cyclohexane. Hydrogen abstraction ability of HexI was much lower than that of BuI. In bulk styrene polymerization, BuI acted as a more efficient initiator than the perester type initiator of *t*-butyl peroxylaurate, keeping high initiator efficiency up to high monomer conversions.

KEY WORDS Radical Trapping / Monoperoxycarbonates / Initiation Mechanism / Decarboxylation /

Hydrogen Abstraction / Initiator Efficiency /

Monoperoxycarbonates are useful initiators for styrene polymerization and used at relatively high temperatures above 100°C. The homolytic cleavage of the O-O bond gives alkoxy and alkoxycarbonyloxy (carbonate) radicals. While much information on the reactions of alkoxy radicals is available,^{1,2} information on carbonate radicals is quite limited,³⁻⁵ particularly at high temperature. Recently, Chateauneuf et al.⁵ determined the absolute rate constants for reactions of carbonate radicals by laser flash photolysis technique. For *n*-propoxycarbonyloxy radicals (*n*-PrOCOO \cdot), the rate constants for the addition to styrene, hydrogen abstraction from cyclohexane, and decarboxylation were reported to be 2.0×10^9 $M^{-1}s^{-1}$, $1.6 \times 10^7 M^{-1}s^{-1}$, and $\leq 1.6 \times 10^5 s^{-1}$, respectively, in CCl₄ at 20°C. This indicates that decarboxylation of carbonate radicals can not compete with addition to styrene at low temperature. However, the reactivity of radicals should be greatly dependent on reaction temperature. To obtain useful information, it is worthwhile to investigate carbonate radical reactivity at high temperature.

We developed a new method for investigating the initiation mechanisms of organic peroxides using 2,4diphenyl-4-methyl-1-pentene (α -methylstyrene dimer, MSD) as a radical trapping agent.⁶ This technique is based on the unique radical chemistry of MSD, that is, addition-fragmentation reactions between free radicals and MSD (eq 1 and 2).⁷ Cumyl radicals ejected from MSD are deactivated by self-reactions (eq 3).





$$\bigcirc - \langle \cdot + \cdot \rangle - \bigcirc \qquad \bigcirc \qquad \bigcirc - \langle \cdot + \cdot \rangle - \bigcirc \qquad (Major) \qquad (3a) \\ & \bigcirc - \langle - + \rangle - \bigcirc \qquad (3b)$$

MSD trapping is outlined in Scheme 1. When organic peroxides decompose in MSD, olefinic compounds (1) having various fragments (X) derived from organic peroxides are produced through addition-fragmentation reactions. By analyzing the trapping products (1), we obtain useful information on the free radical chemistry of organic peroxides. We demonstrated that the double bond reactivity of MSD is about the same as that of styrene.⁶ Therefore, the trapping products are closely related to initiating radicals in styrene polymerization.

We also developed a new method for evaluating hydrogen abstraction (H-abstraction) ability of organic peroxides using MSD trapping (Scheme 2).⁸ When organic peroxides are decomposed in a mixture of MSD and cyclohexane, cyclohexyl radicals produced through H-abstraction by peroxide-derived radicals from cyclohexane are trapped by MSD. The yield of cyclohexyl radical trapping product (2) is regarded as H-abstraction ability of organic peroxides in the presence of styrenic monomers.

MSD trapping is applicable even at high temperature. Thus, it is expected that the reactivity of carbonate





Scheme 1. Outline of MSD trapping.



Scheme 2. Method for evaluating H-abstraction ability of organic peroxides.

radicals at high temperature can be easily studied *via* thermolysis of monoperoxycarbonates in the presence of MSD. This paper describes the initiation mechanisms and hydrogen abstraction ability of useful monoperoxy-carbonate initiators, *OO-t*-butyl *O*-isopropyl peroxy-carbonate (BuI) and *OO-t*-hexyl *O*-isopropyl peroxy-carbonate (HexI), by MSD trapping at 140°C, and initiation performance of BuI in bulk styrene polymerization is presented in comparison with a perester-type initiator.



EXPERIMENTAL

Measurements

GLC analysis was performed with Shimadzu GC-14A and GC-17A gas chromatographs with a flame ionization detector using capillary columns $(15 \text{ m} \times 0.53 \text{ mm} \text{ or } 25 \text{ m} \times 0.25 \text{ mm})$. GC-MS analysis was conducted on a Shimadzu QP5000 under electron impact conditions (70 eV).

Materials

MSD was obtained from NOF Corporation (Nofmer MSD) and used after purification by distillation. BuI, HexI, *t*-butyl peroxylaurate (BuL), *t*-butyl peroxylaurate (BuZ), and *t*-hexyl peroxybenzoate (HexZ) were used as received from NOF Corporation (purity: 98.0, 90.4, 98.2, 98.6, and 96.2%, respectively).

Commercial grade styrene was washed with 2% NaOH and water, and distilled under reduced pressure before use. Cyclohexane was of guaranteed reagent grade.

MSD Trapping Experiments

An aliquot (2 ml) of a 0.02 M solution of BuI or HexI in MSD was charged into a glass ampoule, which was purged with nitrogen, sealed and immersed in a constant temperature bath at 140° C for 5 h. The reaction products

were analyzed by GLC and GC-MS. Typical conditions of GLC analysis were as follows: column, $25 \text{ m} \times 0.25 \text{ mm}$ capillary column of silicon OV-1 (Shimadzu, HR-1); injector temperature, 150° C; detector temperature, 250° C; initial oven temperature, 50° C; initial hold, 10 min; program rate 1, 10° C min⁻¹; middle oven temperature, 150° C; middle hold, 10 min; program rate 2, 10° C min⁻¹; final oven temperature, 250° C; final hold, 10 min; carrier gas, He (0.4 ml min⁻¹); split ratio, 1:18.

GC retention times and MS spectra of trapping products are given below. The MS spectra showed characteristic fragment peaks of 117, 103, 91, and 77 due to the 2-phenylallyl group of MSD.

Isopropyl 2-phenyl-2-propenyl carbonate (1a). GC retention time, 34.7 min; MS (70 eV) m/z 220 (M⁺), 178, 134, 117, 115, 105, 103, 91, 77, and 43.

3-t-Butoxy-2-phenyl-1-propene (**1b**). GC retention time, 27.9 min; MS (70 eV) *m*/*z* 190 (M⁺), 175, 145, 134, 117, 103, 92, 91, 77, 57, and 41.

2-Phenyl-1-butene (1c). GC retention time, 18.9 min; MS (70 eV) m/z 132 (M⁺), 117, 103, 91, 77, 54, and 51.

2-Phenyl-1-hexene (1d). GC retention time, 23.2 min; MS (70 eV) *m*/*z* 160 (M⁺), 145, 131, 118, 117, 103, 91, 78, 77, 65, 51.

7-Hydroxy-7-methyl-2-phenyl-1-octene (1e). GC retention time, 38.0 min; MS (70 eV) m/z 200 (M⁺ – H₂O), 185, 157, 144, 131, 129, 118, 117, 105, 103, 91, 77, 59, and 43.

3-Cyclohexyl-2-phenyl-1-propene (**2**). GC retention time, 36.1 min; MS (70 eV) *m*/*z* 200 (M⁺), 185, 157, 143, 118, 117, 103, 91, 77, 55, and 41.

Polymerization of Styrene

The radical polymerization of styrene was carried out in the presence of 2 mM BuI or BuL in bulk at 120°C in a sealed glass ampoule purged with nitrogen. Percentage conversion was obtained from residual monomer analysis by GLC.

RESULTS AND DISCUSSION

MSD Trapping

The thermal decomposition of BuI and HexI was carried out in MSD at 140°C for 5h under nitrogen. Decomposition percentages were over 99.9%. MSD trapping products were confirmed by GLC and GC-MS. GLC yields of trapping products based on total radicals produced theoretically from peroxides (2 mol of radicals per mol of peroxides) and possible schemes leading to their production are shown in Schemes 3 and 4.

Total trapping yields for BuI and HexI were 79 and 88%, respectively. The somewhat lower yield of BuI was due to the small recovery of the *t*-butoxy moiety. In the case of BuI, a small amount of *t*-butylalcohol (10%) was detected. This indicates hydrogen abstraction by *t*-butoxy radicals to occur. Thus, the actual free radical production efficiency of BuI should be almost the same as that of HexI and close to unity. Possibly, hydrogen abstraction occurs at allylic hydrogens of MSD (eq 4), since allylic hydrogens are easily abstracted by alkoxy radicals.⁹ The reactions of *t*-butoxy radicals with α -methylstyrene at 60°C lead to 15% hydrogen abstraction from allylic hydrogens (85% addition to the double bond).¹⁰



<Carbonate moiety>



<Alkoxy moiety>



Total 78.6%

Scheme 3. Initiation mechanism of BuI at 140°C.



<Carbonate moiety>



<Alkoxy moiety>



Total 87.7%



Carbonate radicals were efficiently trapped by MSD in both cases. If carbonate radicals undergo decarboxylation, isopropoxy radicals should be trapped by MSD (eq 5). However, such trapping could not be detected. These results clearly demonstrate that decarboxylation of carbonate radicals is very slow even at high temperature $(140^{\circ}C)$ and can not compete with addition to the styrenic

$$\searrow 0 \stackrel{O}{\longrightarrow} 0 \stackrel{-CO_2}{\longrightarrow} \searrow 0 \stackrel{MSD}{\longrightarrow} 0 - MS$$
(5)

A previous study of the initiation mechanisms of peresters, BuL and BuZ, in MSD at 140°C showed that lauroyloxy radicals undergo 100% decarboxylation, while benzoyloxy radicals undergo 29% decarboxylation and 71% addition to MSD.¹¹ Thus, it is summarized that decarboxylation rates at 140°C decrease in the following order: aliphatic acyloxy radicals aromatic acyloxy radicals carbonate radicals. This order is consistent with that studied at low temperature. The absolute rate constants for decarboxylation at *ca*. 20°C are reported to be ~10⁹—10¹⁰, ~10⁶, and $\leq 10^5 \, \text{s}^{-1}$, respectively.^{5,12} This rate difference in decarboxylation rates can be reasonably explained due to differences in stability of radicals formed after decarboxylation, *i.e.*, alkyl aryl > alkoxy.

Various reactions were observed for alkoxy radicals, depending on structure. For *t*-butoxy radicals, addition and β -scission occurred with a ratio of 59/41. β -Scission (elimination of *n*-propyl radicals) and 1,5-hydrogen shift (1,5-H shift) were major reactions for *t*-hexyloxy radicals, the ratio of β -scission to 1,5-H shift being 79/21. Previously, we reported the initiation reactions of alkoxy radicals under the same conditions (in MSD at 140°C), where dialkyl peroxides such as di-*t*-butyl peroxide (BuD) and di-*t*-hexyl peroxide (HexD) were used as generators of alkoxy radicals.⁶ The addition/ β -scission ratio for *t*-butoxy radicals was 62/38, and *n*-propyl elimination/ 1,5-H shift ratio for *t*-hexyloxy radicals, 79/21. These ratios are in good agreement with those obtained in this study.

Hydrogen Abstraction Ability

First, H-abstraction ability of BuI and HexI was evaluated by the conventional method (dimer method) measuring dehydrodimers of solvents when organic peroxides are decomposed in a solvent. The thermal decomposition of BuI and HexI was carried out in neat cyclohexane at 150°C. The yield of cyclohexane dimer (dicyclohexyl) was determined by GLC. The results are shown in Table I. There was no significant difference in dimer yields for BuI and HexI, and dimer yields were nearly equal to those of dialkyl peroxides (BuD and HexD).⁸ Since bimolecular self-reactions of cyclohexyl radicals occur by coupling and disproportionation at around 50/50,¹³ the maximum dimer yield is about 50%. Thus, it was found that the radicals generated from monoperoxycarbonates efficiently abstract hydrogen in neat cyclohexane.

H-Abstraction ability of BuI and HexI was evaluated in a mixture of MSD (2.0 M) and cyclohexane (4.7 M) at 140°C according to the method in Scheme 2. The results were compared with those for dialkyl peroxides and peresters (Table II). H-Abstraction ability for BuI and HexI differed considerably (BuI > HexI). The lower H-abstraction ability of *t*-hexyl-derived peroxide is consistent with the results for dialkyl peroxides (BuD > HexD)⁸ and peresters (BuZ > HexZ), due to the faster self-reaction (β -scission and 1,5-shift) of *t*-hexyloxy

Table	I.	Yields of dicyclohexyl from the decomposition
	of	BuI and HexI in cyclohexane at 150°C ^a

Peroxide	Yield of dicyclohexyl ^b	
	0/0	
BuI	42	
HexI	41	
BuD°	42 ^d	
HexD ^e	44 ^d	

^a Initial peroxide concentration, 0.01 M; decomposition percentages, >99.9%. ^b Based on peroxides. ^c Di-*t*-butyl peroxide. ^d Data from ref 8. ^e Di-*t*-hexyl peroxide.

Table II.	Yields of cyclohexyl trapping product (2) from
the de	composition of BuI and HexI in a mixture
	of MSD and cyclohexane at 140°C ^a

	Yield of 2 ^b	
Peroxide	%	
BuI	43	
HexI	15	
BuZ°	46	
HexZ ^d	19	
BuL ^e	29	
BuD	72 ^f	
HexD	14 ^f	

^a Initial peroxide concentration, 0.02 M; decomposition percentages, >99.9%; MSD, 2.0 M; cyclohexane, 4.7 M. ^b 100 × (mol of 2/half mol of peroxides). ^c *t*-Butyl peroxybenzoate. ^d *t*-Hexyl peroxybenzoate. ^e *t*-Butyl peroxylaurate. ^f Data from ref 8.

radicals to give alkyl radicals. Alkyl radicals are poor hydrogen abstractors and readily trapped by MSD before abstracting hydrogen from cyclohexane.

The yield of **2** for BuI is only slightly higher than half of that for BuD, clearly demonstrating that carbonate radicals are little involved in hydrogen abstraction in the presence of MSD and much more active in addition to the styrenic double bond of MSD. For *n*-PrOCOO·, the rate constant for addition to styrene $(2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ was reported to be about 100 times that for hydrogen abstraction from cyclohexane $(1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$ in CCl₄ at 20°C. Although a direct comparison of the present and reported results is difficult due to large differences in reaction temperatures, they are qualitatively consistent.

BuL is a *t*-butyl-derived peroxide, but the H-abstraction ability was much lower than that of BuI and BuZ, due to the lower free-radical production efficiency of BuL compared to BuI or BuZ (see below).

Polymerization of Styrene

Free-radical production efficiency of aliphatic peresters is reduced by cage reactions, that is, bimolecular radical-radical reactions between alkoxy-alkyl radical pairs (Scheme 5).¹⁴ Such reactions are caused by the facile decarboxylation of acyloxy radicals and are greatly influenced by medium viscosity (favorable at high viscosity). The present study shows that decarboxylation of carbonate radicals is very slow even at high temperature, and that free radical production efficiency of monoperoxycarbonates is close to unity in MSD. This





Figure 1. Time-conversion plot of bulk styrene polymerization with Bul or BuL at 120° C: [Initiator]₀ = 2 mM.

strongly suggests that monoperoxycarbonates act as highly efficient initiators for the polymerization of styrene. To confirm this, the effectiveness of BuI for styrene polymerization was compared with that of BuL (aliphatic perester). Figure 1 shows the time-conversion plots of bulk styrene polymerization at 120°C. It is clear that BuI is more effective than BuL, particularly at high monomer conversions. The decomposition rate constants (k_d) of BuI and BuL were almost the same (2.27 × 10⁻⁴ and 2.33 × 10⁻⁴ s⁻¹, respectively, in benzene at 120°C). Therefore, it is obvious that differences in effectiveness of BuI and BuL are due to those in initiator efficiency. That is, BuI keeps efficiency up to high monomer conversion or high viscosity, due to the slow decarboxylation of carbonate radicals or absence of cage reactions.

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