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Radical Formation from the Reaction of Combustion Smoke with Diphenylamine

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We have attempted to examine the effects of radical scavengers, such as amines and phenols, to trap gas-phase radicals produced from the combustion of Poly (methyl methacrylate)(PMMA), which might cause damage to a living body, using an electron spin resonance (ESR) spin-trapping technique.

As a result, diphenylamine did not decrease the amount of radicals but rather increased it. It indicates that under the conditions of this study, gas-phase radicals were hardly trapped by radical scavengers and that the precursors to produce other kinds of radicals can exist.

It was suggested that from the experiments using several peroxides, the precursors should be diacylperoxides produced from the combustion of PMMA.

Keywords: Gas-phase radicals, combustion smoke, precursors, diphenylamine, peroxides, electron spin resonance

INTRODUCTION

It is known that in a fire, toxic materials such as carbon monoxide, nitrogen oxides, hydrogen chloride, formaldehyde and acrylaldehyde are produced from the combustion of combustibles.[1] However, Lowry *et al.* showed that, during the initial stage of combustion, fatal levels of toxic gas-phase radicals might be produced under certain combustion conditions.[2,3] Pryor *et al.* also indicated the production of gas-phase radicals from the combustion of combustibles.[4,5]

Gas-phase radicals are reported to be a new kind of toxic material.[6,7] Kaneko *et al.* detected gas-phase radicals from the combustion smoke of poly(methyl methacrylate)(PMMA).[8] They suggested that PMMA combustion smoke might contain the precursors, possibly trioxides, that could decompose to form radicals.[8,9]

Ohkubo *et al.* showed that gas-phase radicals could initiate the autoxidation of methyl linolate, which was a model compound of biomembranes.[10]

On the other hand, as for suppressing the gas-phase radicals, Furusawa *et al.* showed that the amount of gas-phase radicals was remarkably reduced in the combustion smoke, when amines and halogenated compounds were added to PMMA. They suggested that the formation of

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gas-phase radicals could be suppressed by the combustion products of amines and halogenated compounds.[11]

However, how to suppress the gas-phase radicals once they are produced is not clear. We therefore studied whether or not radical scavengers could directly trap gas-phase radicals. The amount of radicals were measured using the electron spin resonance(ESR) spin-trapping technique.[12]

MATERIALS AND METHOD

Poly(methyl methacrylate) (PMMA), used for the combustion sample, was kindly supplied by Sumitomo Kagaku Co., Ltd.

Diphenylamine (DPA) and 2,6-di-t-butyl-4-methylphenol (BHT), radical scavengers, were obtained from Wako Pure Chemical Industries, Ltd.

α-Phenyl-N-t-butylnitrone (PBN), a spin trap, was obtained from Aldrich Chemical Company, Inc.

Special grade benzene obtained from Wako was purified before use by first washing with concentrated sulfuric acid and then distilling for use as a solvent.

N,N-dimethylaniline and N-methyl-diphenylamine were obtained from Wako, and N-methylaniline was obtained from Tokyo Chemical Industry Co., Ltd.

Lauroyl peroxide(LP), t-butyl peroxybenzonate, t-butyl peroxy isopropyl carbonate, t-butyl peroxy acetate and t-butyl hydroperoxide were obtained from Kayaku Akzo Corporation, and dibenzoylperoxide(BPO) was obtained from Wako.

2,2,6,6-Tetramethyl-4-oxopiperidinooxy was obtained from Aldrich and used to determine the radical concentrations. A cambridge filter (44mm diameter) to trap tars was obtained from Filtrona Instruments & Automation, Ltd.

The combustion of a polymer was conducted according to the described procedures previously.[8,9] A 36mm (outer diameter) × 700mm quartz tube was placed in a 40mm (inner diameter) × 400mm electric furnace maintained at 600°C. A 0.5g sample of material (polymer) in an alumina boat was quickly placed in the center of the quartz tube and then combusted. A mixed gas of O_2 and N_2 was supplied through the quartz tube (500ml mim^{-1}) to support combustion and to carry away all combustion products. The oxygen concentration (21 vol%) was adjusted so as to obtain sufficient gas-phase radicals in the combustion smoke. Part of the combustion smoke containing gas-phase radicals was passed through the cambridge filter to remove most of the tars and particulates. The smoke was then passed through a vessel containing 4ml of benzene for 30s (250ml min^{-1}) using a suction pump, immediately this solution was divided into two parts. One was added to the solution containing radical scavenger, and the other was added to the solution not containing scavenger.

Respective solutions were stirred in order to react the radical scavenger with the smoke containing gas-phase radicals until it was added to 100mM of benzene solution containing PBN to spin-trap the radicals. It was then preserved in a cold medium (−78°C). About 0.5ml of the solution was transferred to a standard cylindrical ESR tube and degassed using a vaccum pump.

Samples were analyzed with ESR at room temperature. ESR spectra were recorded on a JOEL FE1X spectrometer. The microwave power was 5mW, the modulation amplitude was 0.5G and the modulation frequency was 100kHz. A 0.1-s time constant was used with a 4-min scan time and a 50G scan range.

The reaction of peroxide with DPA was conducted as follows. Peroxide was dissolved in benzene and then added to a 10mM benzene solution of DPA and 100mM benzene solution of PBN. This solution was stirred for 5 min at 30°C, preserved in a cold medium, then analyzed with ESR as described above.

RESULTS

The amount of radicals from the combustion of PMMA in the presence of 1mM benzene solution of BHT, during stirring (30min), is the same as that in the absence of BHT.

However, by adding a 1mM benzene solution of DPA, the shape of the obtained ESR spectra seemed to change. By adding a 100mM benzene solution of DPA, although DPA should be a radical scavenger, the amount of radicals increased about three times.

Figure 1 shows typical ESR spectra obtained when the combustion smoke of PMMA was passed through a solution in the absence or the presence of DPA. Hyperfine splitting constants (aN and aH) and areas were calculated from the spectra (Table I). It shows that radical species obtained in the presence of DPA were different from those in the absence of DPA.

The amount of radicals also increased when the combustion smoke was first passed through the benzene, and after 1 hour, a 10mM benzene solution of DPA was added. Also, the amount of radicals increased when the combustion smoke was passed through a benzene solution of PBN containing aromatic amines other than DPA (Table II).

When BPO or LP was added to the benzene solution of DPA, ESR signals of PBN-adducts were observed. The calculated hyperfine splitting constants are shown in Table III.

DISCUSSION

Gas-phase radicals seem to be produced from the precursors formed in the combustion smoke according to the following equation (1).[8,9]

$$\mathrm{ROOOR} \leftrightharpoons \mathrm{ROO}\cdot + \mathrm{RO}\cdot \qquad (1)$$

The aim of our study is to investigate whether radical scavengers, such as BHT or DPA, are suitable for trapping gas-phase radicals that could possibly damage a living body.

However, by adding a 1mM benzene solution of BHT, the amount of radicals did not change compared with that obtained in the absence of BHT. The results of this study indicate that the gas-phase radicals were hardly trapped by the radical scavengers, and that most of them were trapped by PBN to form PBN adducts based on equations (2) and (3).

$$\mathrm{ROO}\cdot + \mathrm{PBN} \rightarrow \mathrm{ROO\text{-}PBN}\cdot \qquad (2)$$

$$\mathrm{RO}\cdot + \mathrm{PBN} \rightarrow \mathrm{RO\text{-}PBN}\cdot \qquad (3)$$

On the other hand, by adding a 100mM benzene solution of DPA, the amount of radicals increased. Also, by adding an aromatic amine, the amount increased. This suggests the existence of other precursors, which might react with aromatic amines like DPA, to produce other kinds of radicals. When DPA was added after 1 hour to the solution containing the smoke, the amount of radicals increased, which indicate the precursors might be stable in benzene.

There is the possibility that the precursors, which are stable in benzene, are taken into a living body by breathing. If the precursors react with a substance such as DPA, it is expected that damage to a living body will increase due to the radicals.

Among the combustion products, peroxides seem to be one possibility by producing radicals by the reaction with aromatic amine such as DPA. To confirm this possibility, we attempted to examine whether radicals could be produced by reacting several peroxides with DPA in benzene. Peroxides, which were stable in benzene, were used because the precursors were stable in benzene as already described. As a result, ESR spectra of PBN-adducts were obtained from the reaction of DPA with BPO and LP having a diacyl group, but were not obtained from that with other peroxides not having a diacyl group (Table III).

Alkyl radicals, obtained from LP, appeared to be produced from the decarboxylation of the lauroylperoxyl radical formed by the reaction of LP with DPA. aN and aH, the hyperfine splitting

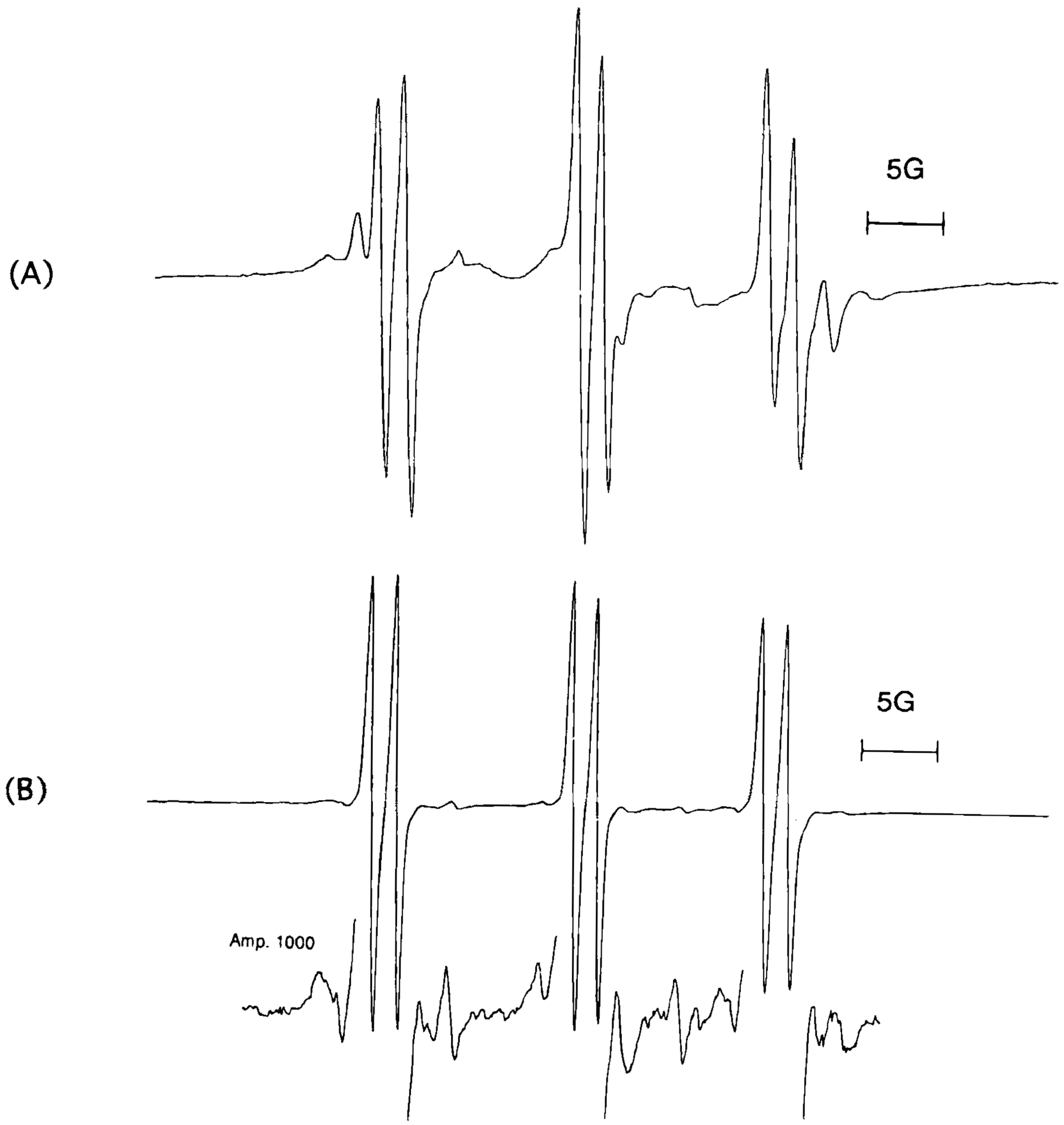

FIGURE 1 Typical ESR spectra obtained when the combustion smoke of PMMA was passed through a solution of PBN (**A**) in the absence and (**B**) in the presence of 50mM DPA. Amplitude was (A) 400 (B) 79.

TABLE I Analysis of the ESR spectra obtained from the combustion smoke of PMMA in the presence and absence of DPA

Solution	aN/Gauss	aH/Gauss	mol%	Radical species[13]
PBN/benzene[a]	13.0	1.7	78	Alkoxyl radical
	14.3	2.4	14	Alkyl radical
	14.9	4.4	8	Unknown
PBN/DPA/benzene[b]	12.9	1.4	94	Acyloxyl radical
		7.8	2	PBN-oxy radical
	14.9	4.4	4	Unknown

[a] ESR spectra corresponds to Figure 1(A)
[b] ESR spectra corresponds to Figure 1(B)

TABLE II Amount of radicals obtained when the combustion smoke of PMMA was passed through a solution of PBN containing aromatic amine

Aromatic amine (mM)	Amount of radicals (10^{-3}mM)[a]
none	5
Diphenylamine (50)	13
N,N-Dimethylaniline (78)	22
N-Methyl-diphenylamine (109)	12
N-Methylaniline (18)	14

[a] Concentration in liquid.

TABLE III Analysis of the ESR spectra obtained from the reaction of peroxide with 10mM solution of DPA in benzene

Peroxide (mM)	aN/ Gauss	aH/ Gauss	Radical species[13]
Dibenzoyl peroxide (1)	12.9	1.4	Benzoyloxyl radical
Lauroyl peroxide (1)	14.7	3.1	Alkyl radical
t-Butyl peroxy acetate (19)	n.d.[a]		
t-Butyl peroxy iso-propyl carbonate (14)	n.d.[a]		
t-Butyl peroxybenzonate (13)	n.d.[a]		
t-Butyl hydroperoxide (44)	n.d.[a]		

[a] ESR spectra of PBN-adducts were not detected.

constants of the radicals observed from the reaction of DPA with BPO, were almost the same as those by the reaction of PMMA combustion smoke with DPA in benzene as shown in Table I.

Thus, the precursors in combustion smoke, to produce other kinds of radicals by the reaction with DPA, seemed to be diacylperoxides such as BPO.

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