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# Vinyl Polymerization 204. Initiation Mechanism of the Radical Polymerization of Vinyl Monomers by p-Methoxy-p′-nitrobenzoyl Peroxide and Tertiary Amines*

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## SUMMARY

A study of the reaction of tertiary amines with p-methoxy-p′-nitrobenzoyl peroxide in the presence of styrene was made in benzene. Anisic acid and p-nitrobenzoic acid were obtained from the reaction product. Using gas chromatography, the molar ratio of the amount of the above two acids was measured and classified into three types, according to the kind of amine used. From the results the reaction mechanism was discussed, and it was concluded that the oxygen which stands adjacent to the p-methoxybenzoyl group may be charged more positively and may be the more predominantly attacked by tertiary amine.

## INTRODUCTION

In this series of papers [1] we have kinetically studied the decomposition of benzoyl peroxide ($Bz_2O_2$) with dialkylanilines, mainly with dimethylaniline (DMA), and also the vinyl polymerization initiated by $Bz_2O_2$-DMA systems. It was concluded that decomposition of $Bz_2O_2$ in the presence of DMA proceeded through formation of a $\pi$-complex intermediate (I) of $Bz_2O_2$ with DMA. The existence of the $\pi$ complex was supported by O'Driscoll and coworkers from UV-spectroscopic measurements [2]. The lone-pair

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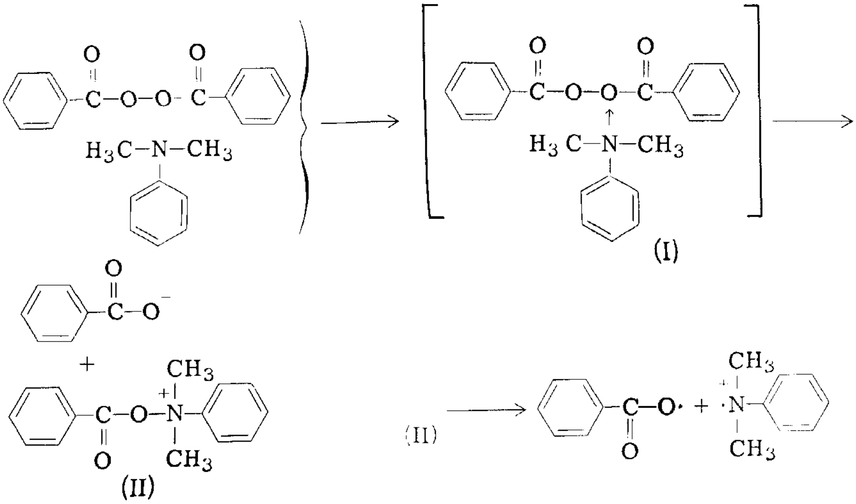
*Part 203 of this series, S. Hayashi and M. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, is in press.

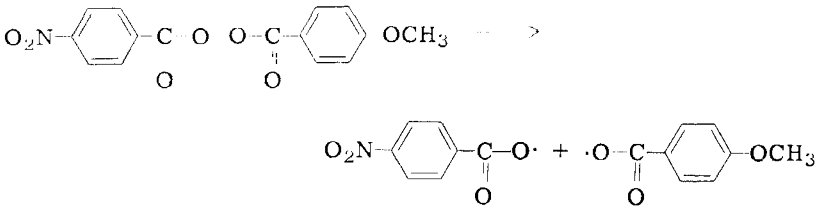
electrons of the nitrogen of DMA coordinate with an oxygen atom of the —O—O— group to give a benzoate anion and N-benzoyloxy anilinium ion (II). The anilinium ion decomposes into a benzoyloxy radical and a anilinium ion radical.


(I)

(II)

The Hammett plot for the rate of decomposition of substituted $Bz_2O_2$ with DMA gave a straight line and its $\rho$ value [3] was positive (0.18). Therefore, the reaction rate increased with positive character of the peroxide bond. We obtained a similar conclusion for radical polymerization initiated with $Bz_2O_2$-DMA systems. In connection with our study mentioned above, O'Driscoll made a study on the rate of decomposition of $Bz_2O_2$ with substituted diethylaniline and concluded that the electron-releasing substituents increased the rate [4]. These observations led to the theory that the lone-pair electrons of nitrogen attacked the positively charged oxygen of the peroxide group.

Polymerization initiated by an unsymmetrically substituted $Bz_2O_2$, that is, p-methoxy-p′-nitrobenzoyl peroxide, was studied in the previous paper [5]. Vinyl polymerization with this peroxide was confirmed to be of a purely radical nature:



The present paper deals with the reaction between p-methoxy-p′-nitrobenzoyl peroxide and DMA or other amines, to determine whether the lone-pair electrons of the nitrogen atom of DMA interact with the more positively charged oxygen atom of the two peroxide oxygens or with the less positively charged oxygen.

## EXPERIMENTAL

Reagents: p-Methoxy-p′-nitrobenzoyl peroxide was synthesized by the reaction of p-nitrobenzoyl chloride with sodium per-p-methoxybenzoate which was prepared by the method for sodium perbenzoate with minor modification [7]. p-Methoxy-p′-nitrobenzoyl peroxide was reprecipitated repeatedly from chloroform with ethyl alcohol or petroleum ether [m.p. 114°C (dec.) (lit. 108°C) [8]].

p-Methoxydimethylaniline was prepared by reaction of p-methoxyaniline with trimethyl phosphate. The product was distilled repeatedly [b.p. 234°C/760 mm Hg (lit. 233-234°C/740 mm Hg) [9]; m.p. 49-49.5°C (lit. 49°C) [9]].

p-Bromodimethylaniline was prepared from the bromination of dimethylaniline in glacial acetic acid diluted with water [m.p. 56°C (lit. 56°C) [10]].

Diacetanilide was prepared by reaction of acetanilide with acetyl chloride. After the product was distilled under a vacuum, it was recrystallized from a ligroin-ethyl alcohol mixture [11] [m.p. 36.5-37°C (lit. 37.5°C)].

Solvents and other amines were purified in the usual manner [12].

Reaction procedure: After the charging of the benzene solution of p-methoxy-p -nitrobenzoyl peroxide and the styrene solution of tertiary amine in a glass tube, the tube was cooled in a dry ice-methanol bath, flushed several times with oxygen-free nitrogen, and sealed under vacuum. Reaction was carried out in a thermostat under shaking. The reaction temperature and time are listed in the tables. The contents were then treated with aqueous alkaline solution. The aqueous layer containing sodium salts of substituted benzoic acids was acidified with diluted hydrochloric acid. The substituted benzoic acids formed were extracted with diethyl ether, and treated further with diazomethane in ether solution to transfer themselves to their methyl esters. Methyl esters thus obtained consisted of a mixture of esters of p-nitrobenzoic acid and anisic acid. The ratio of two esters was measured by gas chromatography, using Yanagimoto GCG-550F apparatus.

## RESULTS

### Effect of the Kind Extracting Agent for Substituted Benzoic Acids on Their Molar Ratios

The results of the reaction of p-methoxy-p′-nitrobenzoyl peroxide with DMA are summarized in Table 1, in which several kinds of alkaline aqueous solutions were used for the extraction of substituted benzoic acids. From Table 1, it can be seen that the ratio of anisic acid formed to p-nitrobenzoic acid formed was almost independent of the molar ratios of DMA to p-methoxy-p′-nitrobenzoyl peroxide between 1 and 9.4; it was also independent of the type of alkaline agent used. Thus 7.5% sodium hydrogen carbonate was used thereafter as the extracting agent.

### Effects of Reaction Temperature on the Molar Ratio of the Recovered Amount of Anisic Acid to that of p-Nitrobenzoic Acid

The results are shown in Table 2; the reaction conditions were kept constant in all cases. The reaction was carried out between 25 and 70°C. The ratio of anisic acid to p-nitrobenzoic acid increased with reaction temperature. The plot of the log of the ratio of anisic acid to p-nitrobenzoic acid against 1/T gave a straight line, as shown in Fig. 1. From the slope, the difference of activation energies of the formations of anisic acid and p-nitrobenzoic acid, $\Delta E_{OCH_3} - \Delta E_{NO_2}$, was calculated by the Arrhenius equation to be 1.0 kcal/mole.

### Reaction of Several Tertiary Amines with p-Methoxy-p′-Nitrobenzoyl Peroxide

The reaction was carried out under the same conditions as described above. The results obtained are summarized in Table 3. As was shown in the case of DMA, the ratio always tended to increase with a rise in the reaction temperature. The results can be classified into three types:

1. In the cases of pyridines and diacetanilide, the molar ratio of anisic acid to p-nitrobenzoic acid resulted in values between 0.23 and 0.40.
2. In the cases of DMA and derivatives, or triethylamine, which are characterized by a $N{-}CH_2$ group, the ratios were between 0.67 and 0.72.
3. Aniline gave a ratio of essentially unity (0.95, 1.02).

## DISCUSSION

The decomposition of p-methoxy-p′-nitrobenzoyl peroxide with tertiary amine may be assumed to proceed through the attack of the

**Table 1.** Effect of the Alkaline Aqueous Solution as Extracting Agents on the Molar Ratio of Anisic Acid to p-Nitrobenzoic Acid in Benzene in Presence of Styrene[a]

| Molar ratio of DMA/p-$OCH_3$-p′-$NO_2$-$Bz_2O_2$ | Reaction temp., °C | Reaction time, hr | Extracting agent | $\frac{\text{Anisic Acid}}{\text{p-Nitrobenzoic acid}}$ |
|---|---|---|---|---|
| 6 | 20 | 5 | 2 *N* NaOH | 0.67 |
| 7 | 20 | 6 | 5% $Na_2CO_3$ | 0.68 |
| 9.4 | 25 | 12 | 7.5% $NaHCO_3$ | 0.66 |
| 2 | 25 | 24 | 7.5% $NaHCO_3$ | 0.60 |
| 1 | 25 | 16 | 7.5% $NaHCO_3$ | 0.60 |
| 1 | 30 | 5 | 7.5% $NaHCO_3$ | 0.67 |

[a] [styrene], 4.94 moles/liter; [p-methoxy-p′-nitrobenzoyl peroxide], $4.5 \times 10^{-2}$ mole/liter.

**Table 2.** Effect of Reaction Temperature on the Molar Ratio of Anisic Acid to p-Nitrobenzoic Acid Formed in the Reaction of DMA with p-Methoxy-p′-nitrobenzoyl Peroxide[a]

| Reaction temp., °C | Reaction time, hr | Anisic acid / p-Nitrobenzoic acid |
|---|---|---|
| 25 | 3 | 0.64 |
| 30 | 2 | 0.67 |
| 40 | 2 | 0.71 |
| 50 | 2 | 0.72 |
| 60 | 2 | 0.75 |
| 70 | 2 | 0.80 |

[a] Solvent, mixture of styrene and benzene: [styrene], 4.94 moles/liter; [DMA] = [p-$OCH_3$-p′-$NO_2$-$Bz_2O_2$], 4.5 × $10^{-2}$ mole/liter.

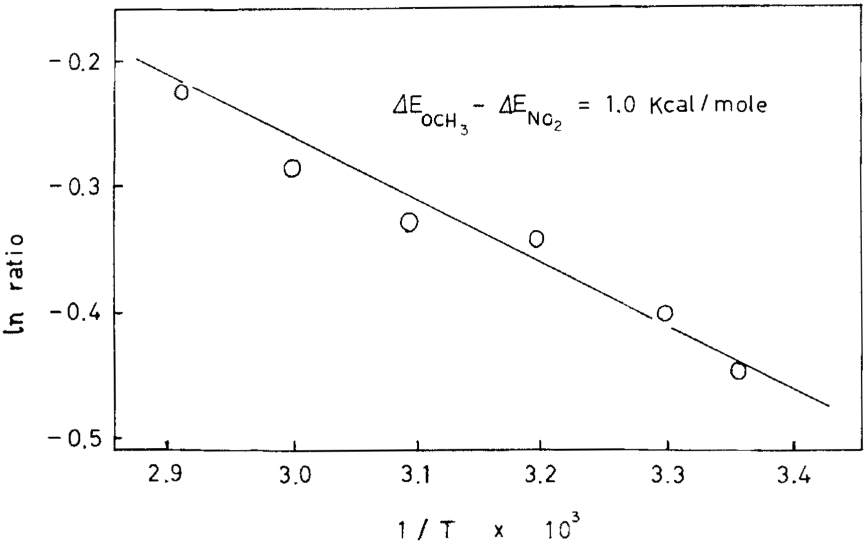


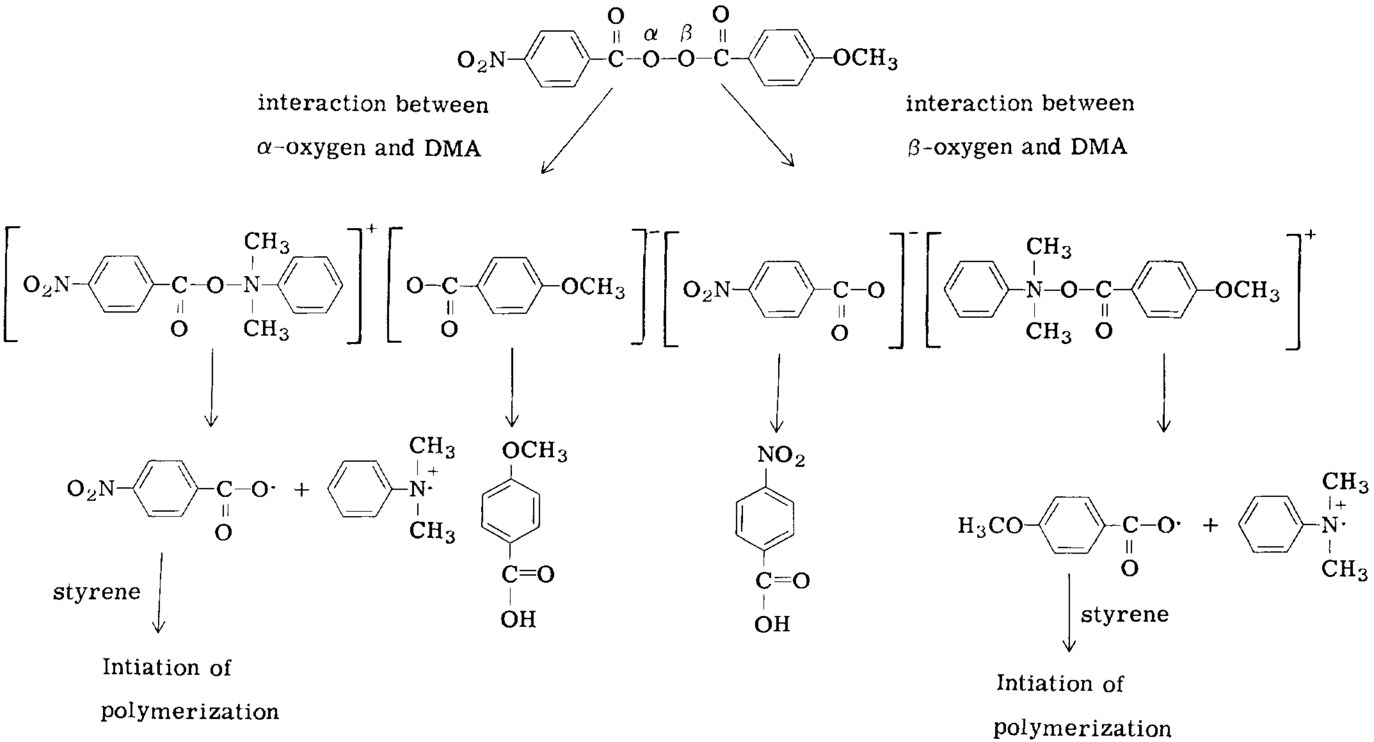
**Fig. 1.** Temperature dependence of the reaction of DMA with p-methoxy-p′-nitrobenzoyl peroxide in a mixture of benzene and styrene.

**Table 3.** Ratio of Anisic Acid to p-Nitrobenzoic Acid in the Reaction of t-Amines with p-$OCH_3$-p'-$NO_2$-$Bz_2O_2$ in the Presence of Styrene[a]

| Amine | Reaction temp., °C | Reaction time, hr | Anisic acid / p-Nitrobenzoic acid |
|---|---|---|---|
| p-$OCH_3$-DMA | 30 | 5 | 0.67 |
| | 60 | 2 | 0.70 |
| p-$CH_3$-DMA | 30 | 5 | 0.67 |
| | 60 | 2 | 0.68 |
| DMA | 30 | 2 | 0.67 |
| | 60 | 2 | 0.75 |
| p-Br-DMA | 30 | 2 | 0.71 |
| | 60 | 2 | 0.77 |
| $Et_3N$ | 30 | 5 | 0.72 |
| Aniline | 30 | 5 | 0.95 |
| | 60 | 5 | 1.02 |
| $\gamma$-Picoline | 30 | 48 | 0.30 |
| | 60 | 25 | 0.34 |
| | 80 | 24 | 0.40 |
| Pyridine | 60 | 25 | 0.23 (0.25) |
| | 80 | 24 | 0.27 |
| Dipyridyl | 60 | 25 | 0.35 |
| Diacetanilide | 60 | 25 | 0.29 |

[a] [t-amine] = [p-$OCH_3$-p'-$NO_2$-$Bz_2O_2$], $4.5 \times 10^{-2}$ mole/liter; [styrene], 4.94 moles/liter.

lone pair of nitrogen to the more positively charged oxygen. Therefore, when the reaction is carried out in the presence of sufficient styrene, the reaction proceeds through the mechanism expressed by the following scheme:


interaction between
α-oxygen and DMA
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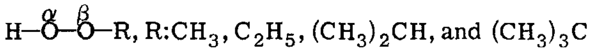
According to this scheme, if a tertiary amine attacks the β-oxygen of the peroxide group, p-nitrobenzoic acid should be obtained predominantly, because the other half of p-methoxybenzoyloxy radical is consumed by the initiation of styrene polymerization. And, vice versa, if the amine attacks the α-oxygen, p-methoxybenzoic acid may be obtained primarily.

From the results obtained above that the molar ratios of anisic acid to p-nitrobenzoic acid formed were always found equal to or less than unity, it could be concluded that the attack of the nitrogen of tertiary amine was oriented predominantly to the β-oxygen atom.

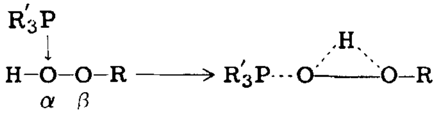
For p-methoxy-p′-nitrobenzoyl peroxide, the β-oxygen which stands adjacent to the p-methoxybenzoyl group is assumed to be charged more positively than the α-oxygen which attaches to the p-nitrobenzoyl group, because the electron-releasing $OCH_3$ group pushes the electrons around the α-oxygen toward the β-oxygen, and the electron-attracting $NO_2$ group pulls the electrons.

It was concluded, as expected, that the lone-pair electrons of nitrogen attack the more positively charged oxygen of the peroxide group. Yonezawa and co-workers recently calculated the formal charge of some alkyl hydrogen peroxides by two kinds of MO methods and concluded that the formal negative charge of α-oxygen was always larger than that of β-oxygen [6]. This result agreed with the above assumption.



$$H{-}\overset{\alpha}{O}{-}\overset{\beta}{O}{-}R,\ R{:}\,CH_3,\ C_2H_5,\ (CH_3)_2CH,\ \text{and}\ (CH_3)_3C$$

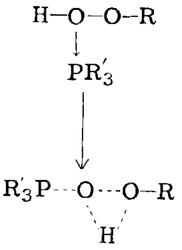
In 1956 Greenbaum and Denney [13] carried out the decomposition of p-methoxy-p′-nitrobenzoyl peroxide, in which one oxygen of the two carbonyl oxygens was labeled with $^{18}O$, in the presence of tri-n-butyl phosphine. They concluded that phosphorous attacked the α-oxygen of the peroxide group, assuming that α-oxygen was charged more positively than β-oxygen. Their conclusion would not agree with ours. In 1960 Denney and co-workers [14] studied the mechanism of the reaction of hydroperoxides with tri-n-butyl phosphine and proposed the following transition state:

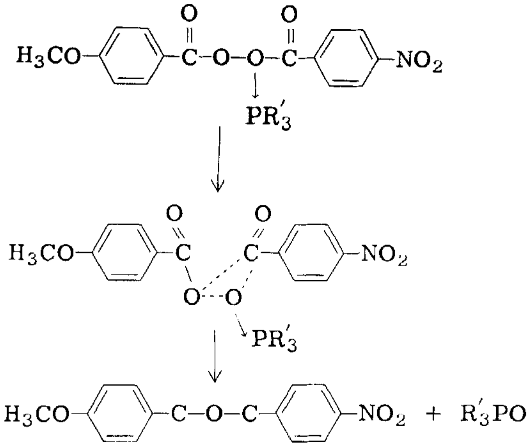


As to the attack of phosphor on the α-oxygen of R—O—O—H, Yonezawa and co-workers stated that the reaction was a nucleophilic reaction of the tri-n-butyl phosphine to the hydroperoxide, and thus that the reaction site of the peroxide group should be the oxygen having the larger delocalizability.

However, an opposite consideration may be possible:
The present authors assume that tri-n-butyl phosphine reacts with

hydroperoxide and with p-methoxyl-p′-nitrobenzoyl peroxide through the following analogous mechanisms:





This consideration, in which tri-n-butyl phosphine behaves as an electrophilic reagent, agrees well with the result of the formal charge of R—O—O—H calculated by Yonezawa et al., and also with our results of the decomposition reaction of p-methoxy-p′-nitrobenzoyl peroxide with tertiary amine.

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