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Tsuneyuki Sato[a]; Kunio Hibino[a]; Takayuki Otsu[a]
[a] Department of Applied Chemistry Faculty of Engineering, Osaka City University Sugimoto-cho, Osaka, Japan

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# Initiation Mechanism of Alternating Copolymerization of Styrene with Some Electron-Accepting Monomers in the Presence of Zinc Chloride by Means of Spin Trapping Technique

TSUNEYUKI SATO, KUNIO HIBINO, and TAKAYUKI OTSU

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan

## ABSTRACT

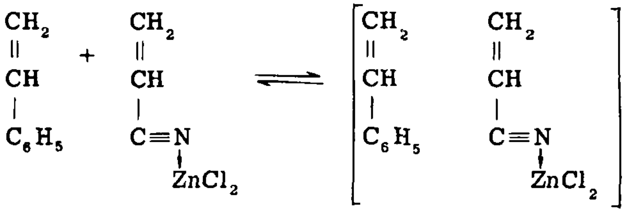
The initiation mechanism of spontaneous alternating copolymerizations of styrene (St) and some electron-accepting monomers such as methyl methacrylate (MMA), methyl acrylate (MA), methacrylonitrile (MAN), and acrylonitrile (AN) in the presence of $ZnCl_2$ was studied by the spin trapping technique, in which 2-methyl-2-nitrosopropane (BNO) was used as a spin trapping reagent. When this technique was applied to the alternating copolymerization systems of St-MMA-$ZnCl_2$, St-MA-$ZnCl_2$, and St-MAN-$ZnCl_2$, the 2-phenylvinyl radical ($\cdot CH{=}CH{-}C_6H_5$) was trapped as nitroxide. The structure of this nitroxide, which showed a large coupling constant (19~20 G) by β-hydrogen, was confirmed by comparison with the result of authentic experiment. Accordingly it was concluded that this nitroxide was formed through proton migration from the St cation radical to the acceptor monomer anion radical in the charge- or electron-transfer complex, followed by reaction with BNO.

In the St-AN-$ZnCl_2$ system, however, a nitroxide derived from a cyclic radical was observed together with the nitroxide from 2-phenylvinyl radical. This cyclic radical seemed to be produced via the Diels-Alder adduct between St and AN.

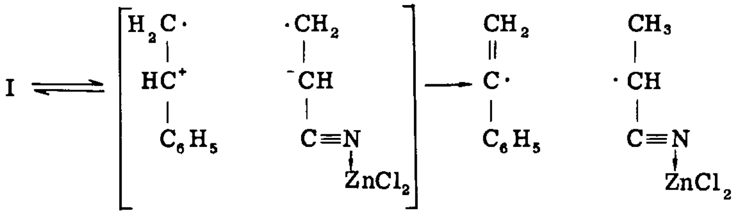
## INTRODUCTION

Some weak electron-accepting monomers such as acrylonitrile (AN), methacrylonitrile (MAN), methyl acrylate (MA), and methyl methacrylate (MMA) have been known to copolymerize with electron-donating olefins such as butadiene, isoprene, styrene (St), and α-methylstyrene (α-MSt) in the presence of Lewis acids ($ZnCl_2$, $SnCl_4$, $(C_2H_5)_nAlCl_{3-n}$, etc.) to produce alternating copolymers [1-3]. Especially, in the systems containing $ZnCl_2$ or $(C_2H_5)_nAlCl_{3-n}$, the copolymerizations have been found to proceed at a considerable rate even in the absence of radical initiator. In these cases the charge-transfer complex formed between the olefin and the polar monomer complexed with Lewis acid has been thought to participate in the initiation and propagation of these copolymerizations.

Yabumoto et al. [1] have found that the copolymerization of St with AN in the presence of $ZnCl_2$ gives an alternating copolymer, and have proposed the initiation mechanism shown in Eq. (1): a charge transfer complex (I) is first formed between electron-donating St monomer and electron-accepting AN monomer complexed with $ZnCl_2$, and subsequently it is transformed to the electron-transfer complex (II) form, from which the transfer of a proton from the St unit to the AN unit occurs to give the initiating radicals III and IV.



charge transfer complex (I)



$$\mathrm{I} \rightleftharpoons \left[\begin{matrix} \mathrm{H_2C\cdot} \\ | \\ \mathrm{HC^+} \\ | \\ \mathrm{C_6H_5} \end{matrix} \quad \begin{matrix} \mathrm{\cdot CH_2} \\ | \\ \mathrm{^-CH} \\ | \\ \mathrm{C{\equiv}N} \\ \downarrow \\ \mathrm{ZnCl_2} \end{matrix}\right] \longrightarrow \begin{matrix} \mathrm{CH_2} \\ \| \\ \mathrm{C\cdot} \\ | \\ \mathrm{C_6H_5} \end{matrix} \quad \begin{matrix} \mathrm{CH_3} \\ | \\ \mathrm{\cdot CH} \\ | \\ \mathrm{C{\equiv}N} \\ \downarrow \\ \mathrm{ZnCl_2} \end{matrix} \qquad (1)$$

(II) (III) (IV)

Later, Gaylord proposed [4] a different initiation mechanism which involves a hydrogen abstraction via either a six-membered cyclic transition state or the formation of a carbene structure. However, there is no supporting evidence for these mechanisms.

We have recently applied the spin trapping technique to detect and identify the intermediate radical species produced from various initiator systems such as triethylboron/oxygen [5], benzoyl peroxide/dimethylaniline [6], and N-chlorosuccinimide/p-toluenesulfonic acid [7]. More recently we have also applied this technique to spontaneous alternating copolymerization of some donor monomers with acceptor monomers in the absence of Lewis acids [8]. This paper is concerned with the results obtained by means of spin trapping technique to clarify the initiating radical species produced from spontaneous alternating copolymerizations of St with some electron-accepting monomers such as MMA, MA, MAN, and AN in the presence of $ZnCl_2$.

## EXPERIMENTAL

### Materials

2-Methyl-2-nitrosoprane (BNO) was prepared by the oxidation of tert-butylamine by m-chloroperbenzoic acid according to the method of Perkins [9].

Di-tert-butyl peroxalate (DBPOX) was prepared by the reaction of oxalyl chloride with tert-butyl hydroperoxide according to the method of Bartlett [10].

Tri-n-butyltin hydride was obtained by the reduction of tri-n-butyltin chloride with lithium aluminum hydride [11].

Solvents, monomers, and $ZnCl_2$ were used after purification by ordinary methods.

### Measurement of ESR Spectra

A solution containing electron-accepting monomer—$ZnCl_2$ complex was added to the St monomer, and an aliquot of this was introduced in the ESR tube which was placed in the spin trapping reagent. This tube was then degassed and sealed under vacuum. After an appropriate reaction time, the ESR spectrum was recorded with a JES-ME-3X spectrometer equipped with 100 kHz field modulation.

## RESULTS AND DISCUSSION

### St-MMA, MA, and MAN Systems

To detect and identify the initiating radical species produced in spontaneous alternating copolymerizations, the reaction of MMA with St in the presence of $ZnCl_2$ was carried out in the presence of BNO at room temperature. Figure 1 shows an ESR spectrum obtained from this reaction mixture. This spectrum is assigned to a mixture of two nitroxides which was obtained from the reaction of BNO with two different intermediate radicals produced: the nitroxide (V-1), which shows a hfs with a triplet-doublet-doublet ($A_N$ = 14.9 G, $A_{\beta\text{-}H}$ = 20.2 G, $A_{\gamma\text{-}H}$ = 0.7 G), and the nitroxide (VI-1), which shows a hfs with triplet-doublet ($A_N$ = 14.7 G, $A_{\beta\text{-}H}$ = 3.8 G).

Figures 2 and 3 show the ESR spectra observed from the systems of St-MA-$ZnCl_2$-BNO and St-MAN-$ZnCl_2$-BNO, respectively. Similarly to the above system, two nitroxides (V-2 and VI-2, and V-3 and VI-3, respectively) were produced. Their coupling constants are as follows: nitroxides V-2 ($A_N$ = 14.9 G, $A_{\beta\text{-}H}$ = 19.8 G, $A_{\gamma\text{-}H}$ = 0.7 G), VI-2 ($A_N$ = 14.6 G, $A_{\beta\text{-}H}$ = 3.2 G), V-3 ($A_N$ = 14.9 G, $A_{\beta\text{-}H}$ = 19.7 G, $A_{\gamma\text{-}H}$ = 0.7 G), and VI-3 ($A_N$ = 14.8 G, $A_{\beta\text{-}H}$ = 3.3 G).

It is interesting to note that nitroxides V-1 to V-3 produced from the above three systems show quite large coupling constants of β-hydrogen.

Although the coupling constants of β -hydrogen, $A_{\beta\text{-}H}$, of the nitroxides derived from the reaction of BNO with alkyl radicals carrying a hydrogen at α-position are in general known to be in the range of 1 to 5 G, those of the observed nitroxides (V-1 to V-3) show abnormally large coupling constants (19 to 20 G). These nitroxides have not been found in the reactions of BNO with alkyl

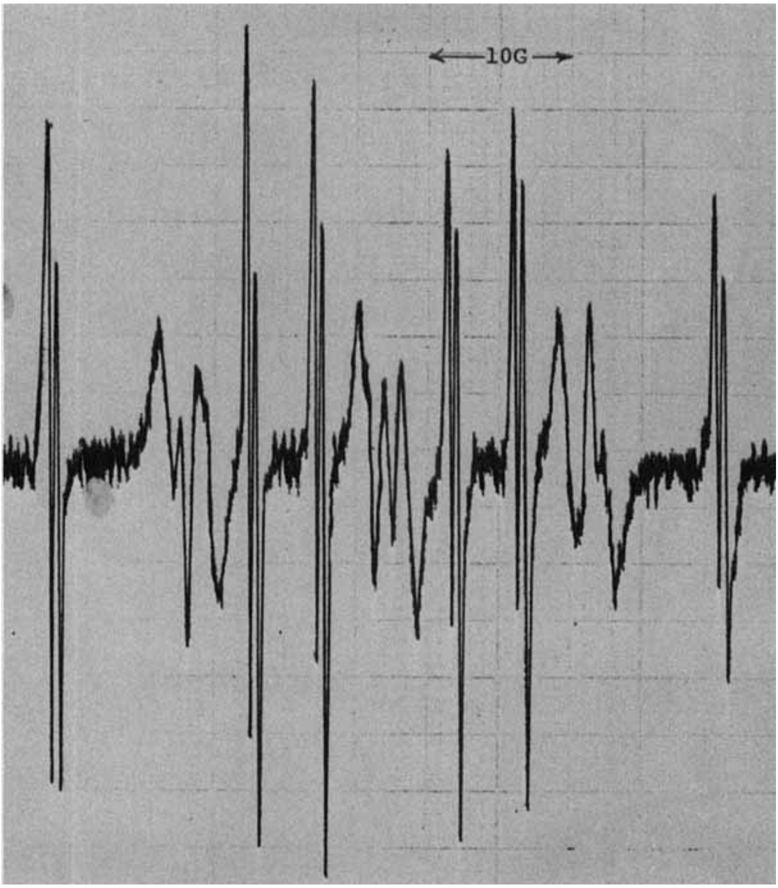


FIG. 1. ESR spectrum obtained in the reaction of the MMA-St-$ZnCl_2$-BNO system at room temperature for 24 hr. MMA, 0.5 ml; St, 0.5 ml; $ZnCl_2$, 3 mg; [BNO] = 0.01 mole/liter.

radicals, but they may be produced from those with a vinyl-type radical.

To obtain further evidence of whether a vinyl-type radical is formed in these systems, the spin trapping technique was applied to a model reaction of DBPOX, $(n\text{-}Bu)_3SnH$, and β-bromostyrene in the presence of BNO. From this reaction a 2-phenylvinyl radical is

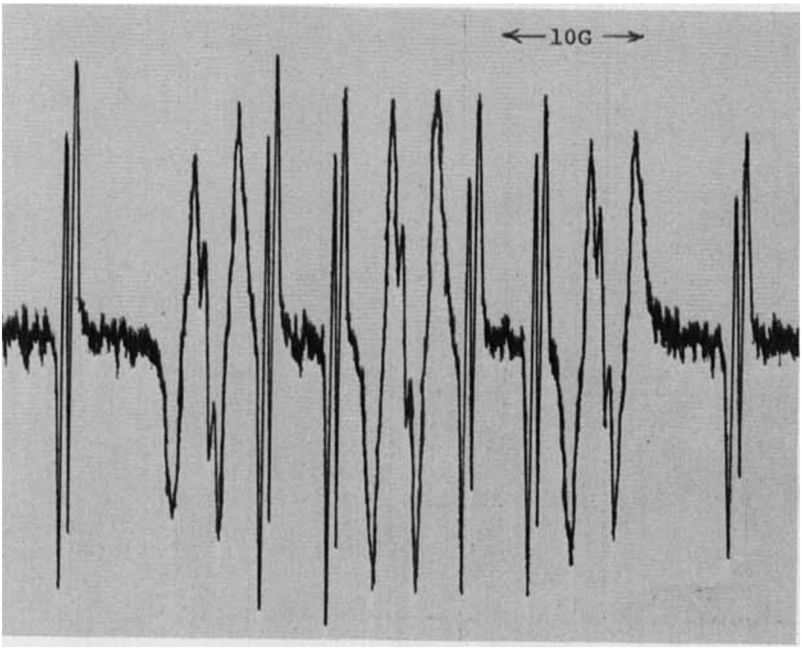


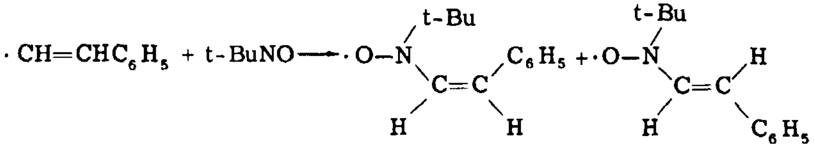
FIG. 2. ESR spectrum obtained in the reaction of the MA-St-$ZnCl_2$-BNO system at room temperature for 25 hr. MA, 0.5 ml; St, 0.5 ml; $ZnCl_2$, 3 mg; [BNO] = 0.005 mole/liter.

expected to be formed first, and then reacted with BNO to give the nitroxide, according to

$$(t\text{-}BuOOOC)_2 \longrightarrow 2\ t\text{-}BuO\cdot + 2CO_2$$

$$t\text{-}BuO\cdot + (n\text{-}Bu)_3SnH \longrightarrow t\text{-}BuOH + (n\text{-}Bu)_3Sn\cdot \qquad (2)$$

$$(n\text{-}Bu)_3Sn\cdot + BrCH{=}CH{-}C_6H_5 \longrightarrow \cdot CH{=}CHC_6H_5 + (n\text{-}Bu)_3SnBr$$



$$\cdot CH{=}CHC_6H_5 + t\text{-}BuNO \longrightarrow \cdot O{-}N(t\text{-}Bu){-}CH{=}CH{-}C_6H_5 + \cdot O{-}N(t\text{-}Bu){-}CH{=}CH{-}C_6H_5$$

(VII) (VIII)

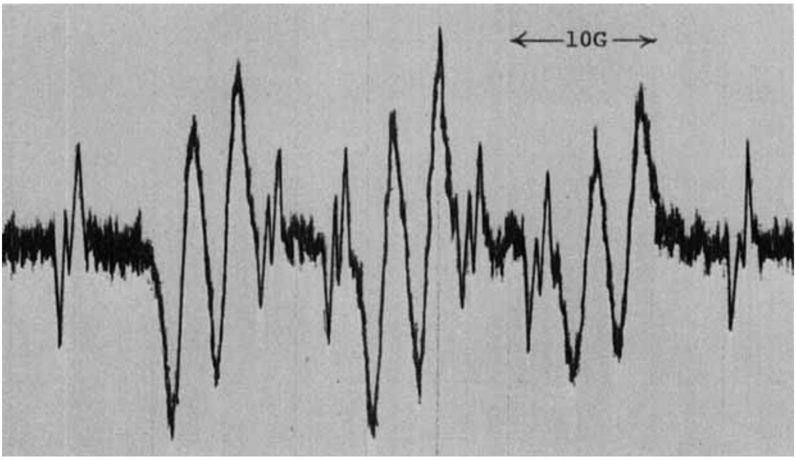


FIG. 3. ESR spectrum obtained in the reaction of the MAN-St-$ZnCl_2$-BNO system at room temperature for 2 hr. MAN, 0.5 ml; St, 0.5 ml; $ZnCl_2$, 3 mg; [BNO] = 0.005 mole/liter.

The ESR spectrum obtained from this reaction mixture is shown in Fig. 4. As can be seen, the spectrum obtained with a triplet-doublet-triplet ($A_N$ = 14.9 G, $A_{\beta\text{-H}}$ = 19.6 G, and $A_{\gamma\text{-H}}$ = 0.8 G) is almost the same as those of Figs. 1 to 3, and the observed coupling constants, $A_{\beta\text{-H}}$, of $\beta$-hydrogen is quite large and similar to those of V-1, V-2, and V-3 in the above system. These results indicate that the nitroxides V-1, V-2, and V-3 are the same, and that they are formed by the reaction of BNO with an identical vinyl-type radical, 2-phenylvinyl radical (IX), which forms from the St monomer side. The observed triplet by $\gamma$-hydrogen in this model reaction system (Fig. 4) might result from an overlap of two doublets by $\gamma$-hydrogens of cis-(VII) and trans-nitroxides (VIII). [a cis and trans (16:84) mixture of $\beta$-bromostyrene was used]. Therefore, in the present copolymerization systems, only one vinyl-type radical either in cis- or trans-isomer form might be produced by a stereospecific reaction in the charge or electron-transfer complex, and then reacted with BNO without isomerization:

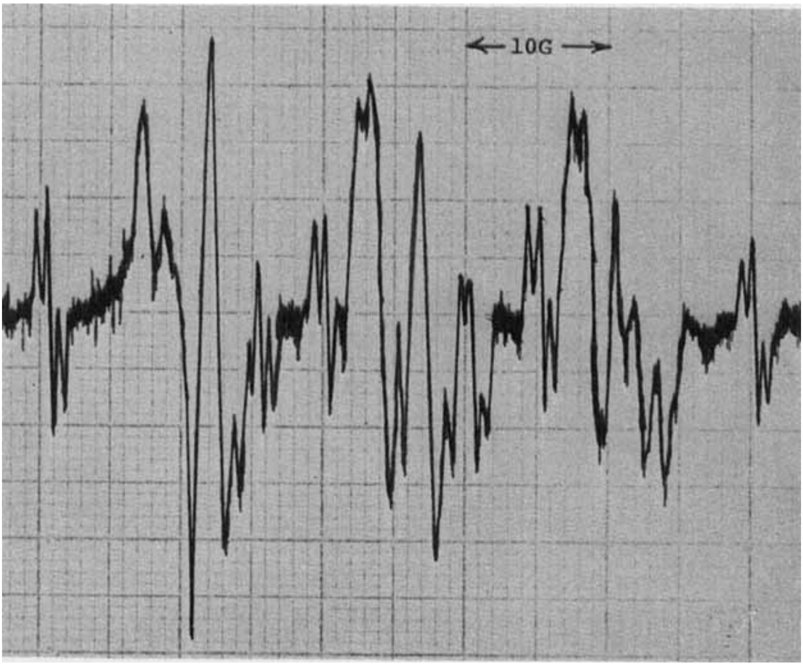
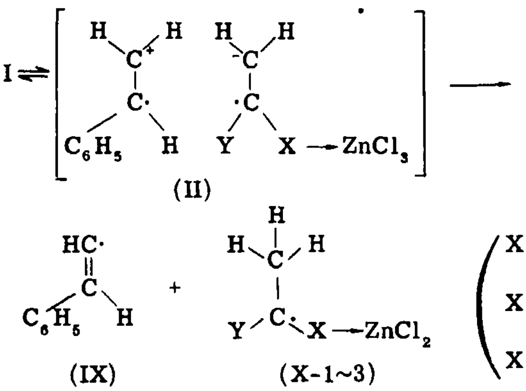


FIG. 4. ESR spectrum obtained in the reaction of the β-bromostyrene–(n-Bu)$_3$SnH–DBPOX–BNO system at room temperature for 1 hr. β-Bromostyrene, 0.2 ml; (n-Bu)$_3$SnH, 0.2 ml, [DBPOX] = 0.05 mole/liter; [BNO] = 0.05 mole/liter.



(3)

X-1: X = $COOCH_3$, Y = $CH_3$

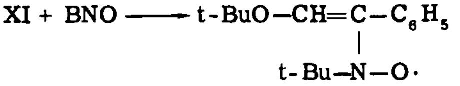
X-2: X = $COOCH_3$, Y = H

X-3: X = CN, Y = $CH_3$

Furthermore, Fig. 5 shows the ESR spectrum of the reaction mixture of phenylacetylene with DBPOX in the presence of BNO. This spectrum is assigned to the 1-N-t-butyl-2-butoxystrenyl-1-nitroxide (XII, $A_N$ = 14.6 G and $A_{\beta\text{-}H}$ = 2.4 G) which is obtained from the addition reaction of the t-butoxy radical to phenylacetylene, followed by reaction with BNO according to

$$t\text{-}BuO\cdot + CH{\equiv}CC_6H_5 \longrightarrow t\text{-}BuO-CH=\dot{C}-C_6H_5$$

(XI)

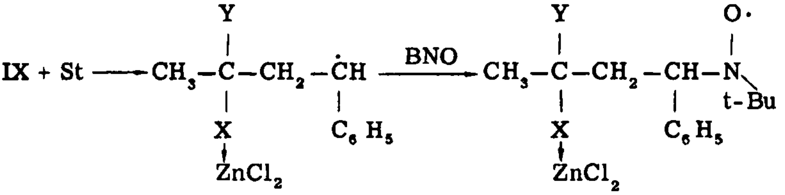


$$XI + BNO \longrightarrow t\text{-}BuO-CH=\underset{\substack{| \\ t\text{-}Bu-N-O\cdot}}{C}-C_6H_5 \qquad (4)$$

(XII)

The ESR spectrum (Fig. 5) is quite different from that of Figs. 1 to 3, from which it is clear that an intermediate radical obtained from the St-electron accepting monomers-$ZnCl_2$-BNO systems is the radical IX, not XI. This result strongly supports the reaction scheme of Eq. (3).

On the other hand, $A_N$ values (14.6 to 14.8 G) of nitroxide VI-1 to VI-3 and the fact that MMA and MAN having no $\alpha$-hydrogen gave also the nitroxides carrying a $\beta$-hydrogen, similarly to MA, suggest that the nitroxides VI-1 to VI-3 are also derived from St. Radicals X-1 to X-3 formed in Eq. (3) might react more easily with St than BNO to produce radicals (XIII-1 to XIII-3), which were trapped by BNO (Eq. 5), to form nitroxides VI-1 to VI-3 observed in Figs. 1 to 3.



$$IX + St \longrightarrow CH_3-\underset{\substack{| \\ X \\ \downarrow \\ ZnCl_2}}{\overset{\substack{Y \\ |}}{C}}-CH_2-\underset{\substack{| \\ C_6H_5}}{\dot{C}H} \xrightarrow{BNO} CH_3-\underset{\substack{| \\ X \\ \downarrow \\ ZnCl_2}}{\overset{\substack{Y \\ |}}{C}}-CH_2-\underset{\substack{| \\ C_6H_5}}{CH}-\overset{\substack{O\cdot \\ |}}{N}\diagdown t\text{-}Bu \qquad (5)$$

(XIII-1~3) (VI-1~3)

1: X = $COOCH_3$, Y = $CH_3$
2: X = $COOCH_3$, Y = H
3: X = CN, Y = $CH_3$

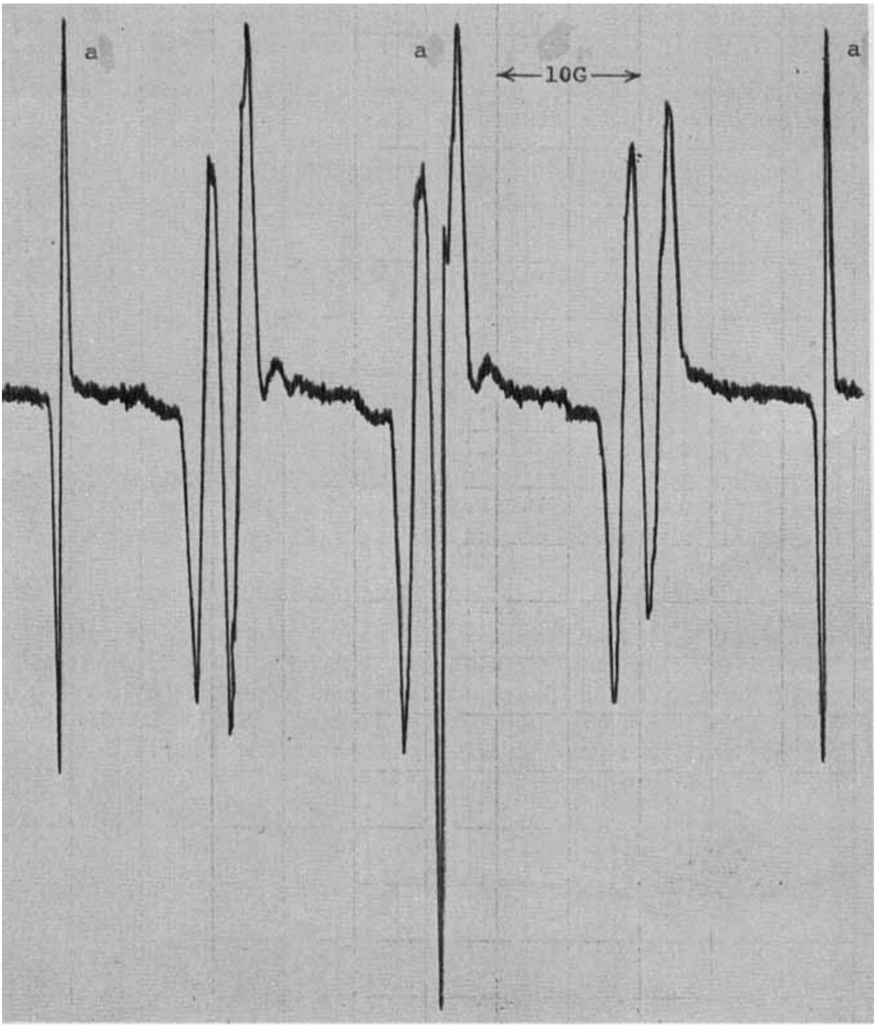


FIG. 5. ESR spectrum obtained in the reaction of the phenylacetylene-DBPOX-BNO system at room temperature for 2 hr. [DBPOX] = 0.4 mole/liter; [BNO] = 0.02 mole/liter. a indicates the peaks due to tert-butoxy–tert-butylnitroxide.

## St-AN System

Figure 6 shows the ESR spectrum observed from the St-AN-$ZnCl_2$-BNO system. This spectrum is quite different from those observed from the St-MMA, MA, and MAN-$ZnCl_2$-BNO systems (Figs. 1 to 3). From Fig. 6, a new spectrum with a fine hfs is observed together with those due to the nitroxides V-4 ($A_N = 14.9$ G, $A_{\beta\text{-H}} = 20.2$ G, $A_{\gamma\text{-H}} = 0.7$ G) and VI-4 ($A_N = 14.7$ G, $A_{\beta\text{-H}} = 3.8$ G). The absorption of the spectrum due to the new nitroxide is found to increase with an increasing reaction time and the concentration of $ZnCl_2$ as compared with those of the nitroxides V-4 and VI-4 (Fig. 7).

To confirm the structure of the new nitroxide, the ESR determinations were attempted of the reaction mixtures of the hydrogen abstraction reactions of 9,10-dihydrophenanthrene and tetraline with DBPOX in the presence of BNO. The ESR spectra observed are shown in Figs. 8 and 9. The observed spectra, which are assigned as the nitroxides XIV and XV, respectively, are very close to that of the nitroxide observed in Fig. 6.

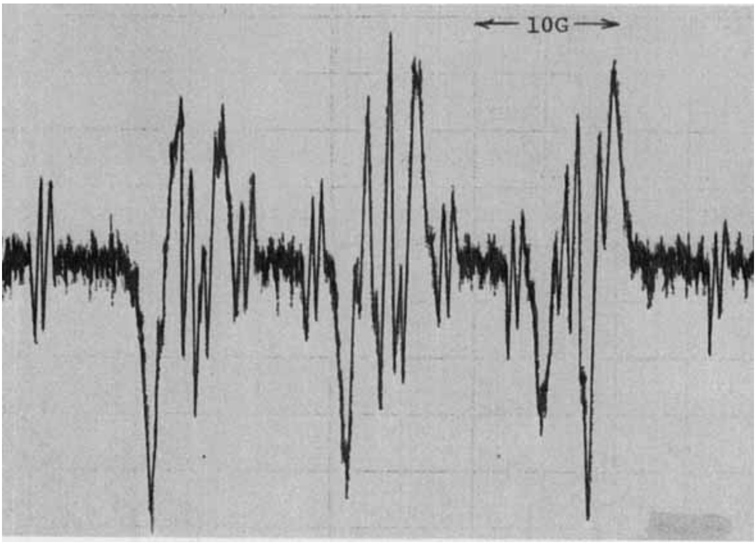


FIG. 6. ESR spectrum obtained in the reaction of the AN-St-$ZnCl_2$-BNO system at room temperature for 3.5 hr. AN, 0.5 ml; St, 0.5 ml; $ZnCl_2$, 3 mg; [BNO] = 0.005 mole/liter.

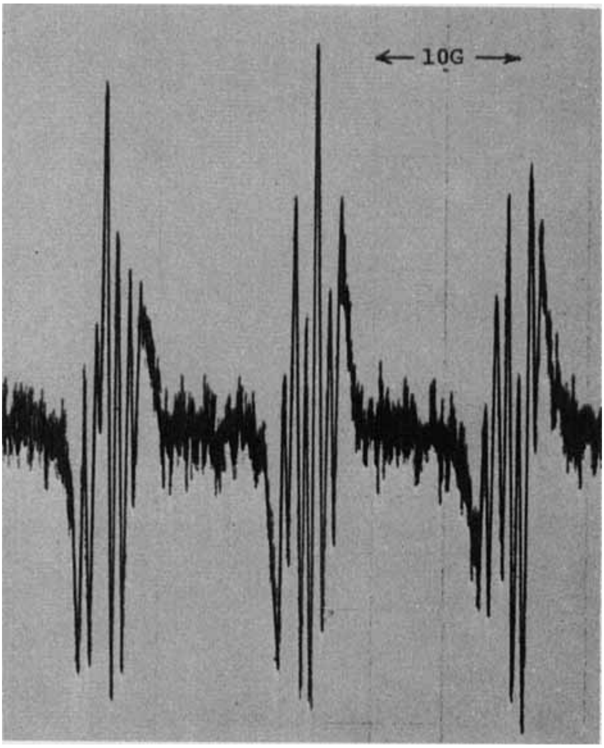
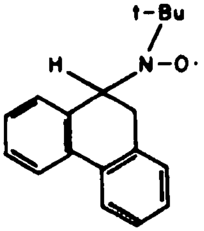
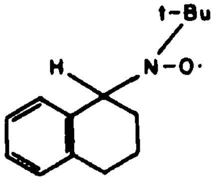


FIG. 7. ESR spectrum obtained in the reaction of the AN-St-$ZnCl_2$-BNO system at room temperature for 4 hr. AN, 0.5 ml; St, 0.5 ml; $ZnCl_2$, 9 mg; [BNO] = 0.05 mole/liter.



(XIV)



(XV)

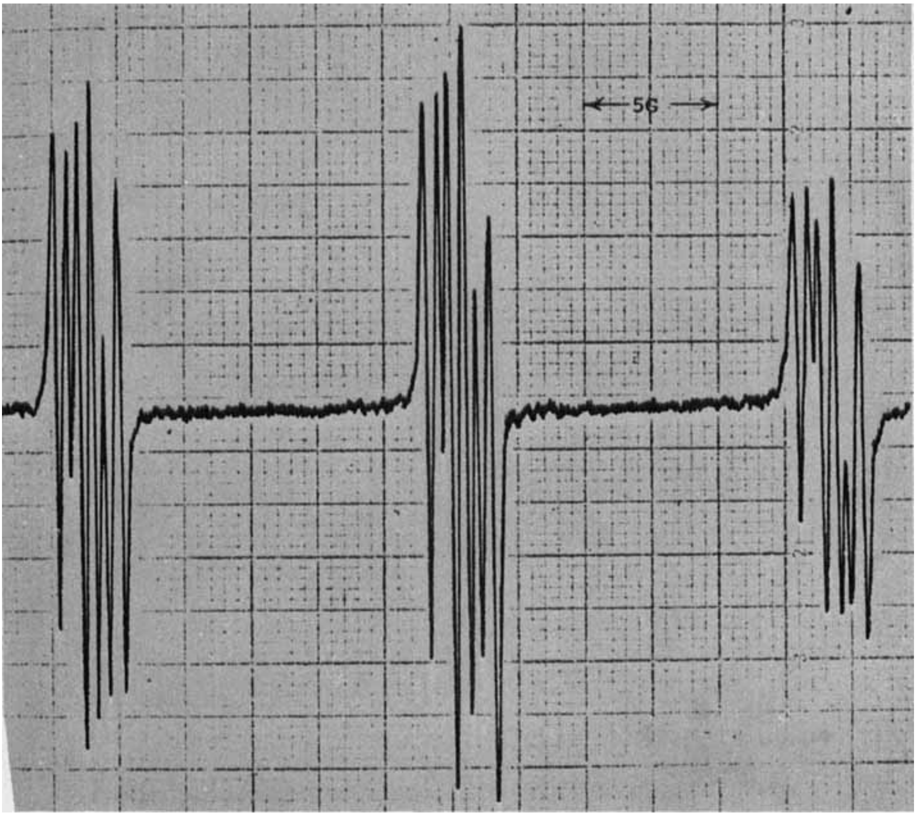


FIG. 8. ESR spectrum obtained in the reaction of the 9, 10-dihydrophenanthrene-DBPOX-BNO system at room temperature for 2 hr. 9, 10-Dihydrophenanthrene, 0.1 g; benzene, 0.5 ml; [DBPOX] = 0.04 mole/liter; [BNO] = 0.01 mole/liter.

It has been well known in the thermal polymerization of St [12] that the initiating radical is produced through the formation of the Diels-Alder adduct between two St molecules. Of course, electron-accepting vinyl monomers such as AN are excellent as dienophiles. Further, the Diels-Alder reaction has been also known to be accelerated by the presence of a Lewis acid [13]. In the present St-AN system, therefore, the new nitroxide seems to be obtained by the reaction of BNO with 1-cyanotetraline-4-radical (XVI) produced

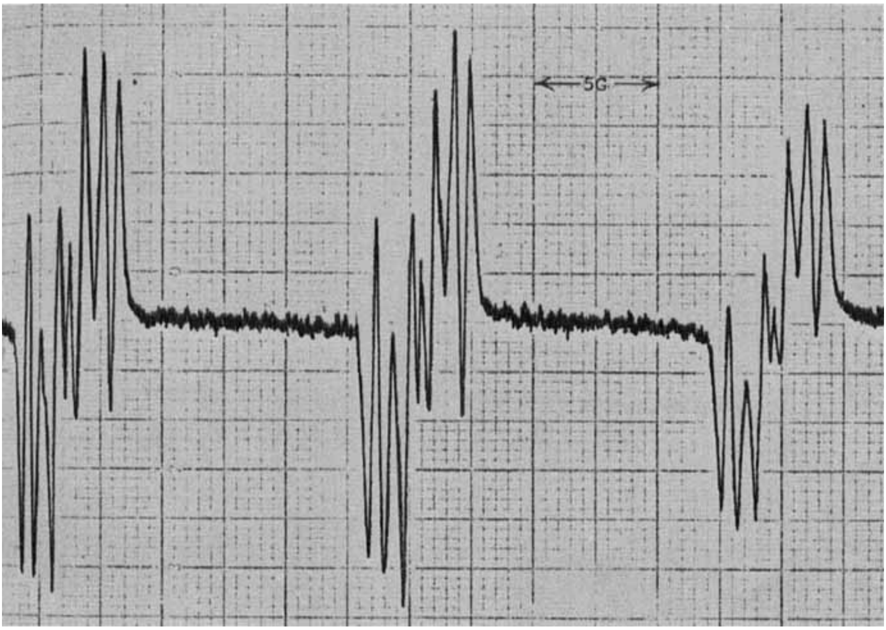
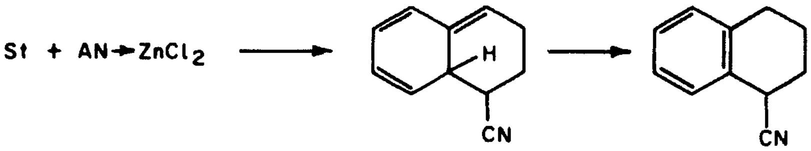


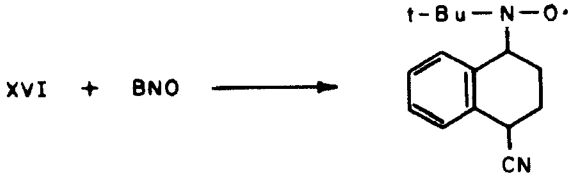
FIG. 9. ESR spectrum obtained in the reaction of the tetralin-DBPOX-BNO system at room temperature for 2 hr. [DBPOX] = 0.04 mole/liter; [BNO] = 0.02 mole/liter.

through hydrogen abstraction from a Diels-Alder adduct between St and AN-$ZnCl_2$:



(6)

(XVI)



(XVII)

However, the formation of the nitroxides V-4 and VI-4 also suggests that the production of the intermediate radicals [IX and X-4 (X = CN, Y = H)] by Eq. (3) occurs concurrently with Eq. (6) in this system. The observed difference in radicals trapped between the MMA, MA, and MAN systems and the AN system seems to take place due to its activity as a dienophile.

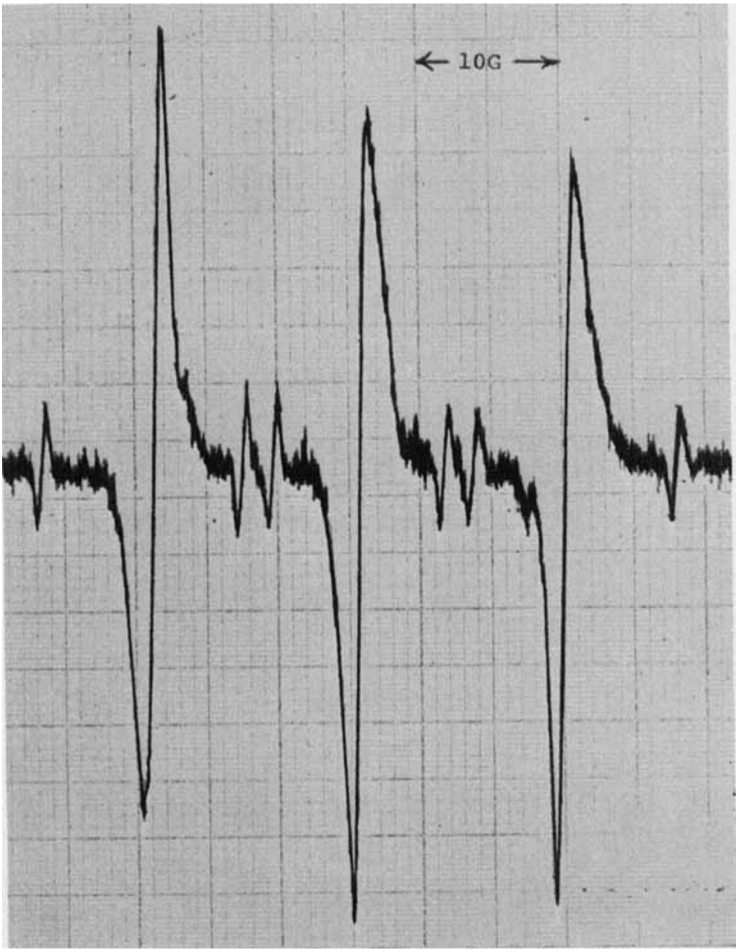
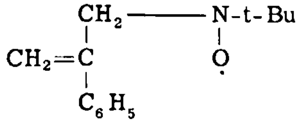


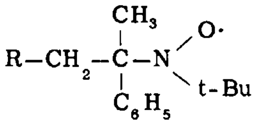
FIG. 10. ESR spectrum obtained in the reaction of the MA—α-MSt—$ZnCl_2$ system at room temperature for 2.5 hr. MA, 0.5 ml; α-MSt, 0.5 ml/ $ZnCl_2$, 3 mg; [BNO] = 0.005 mole/liter.

### α-Methylstyrene (α-MSt)—MA System

Figure 10 shows the ESR spectrum observed in the α-MSt—MA—$ZnCl_2$—BNO system. This spectrum is different from that observed in the St-MA-$ZnCl_2$-BNO system (Fig. 2) and is assigned as a mixture of two nitroxides, XVIII ($A_N = 14.4$ G, $A_{\beta\text{-}H} = 8.3$ G) [authentic nitroxide; $A_N = 14.5$ G, $A_{\beta\text{-}H} = 8.3$ G (in methylacetate—α-MSt 50:50 v/v)] and XIX ($A_N = 14.5$ G), which was formed by addition of some radical (R·) to α-MSt:

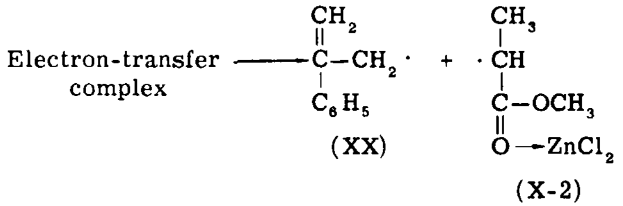


(XVIII)



(XIX)

The nitroxide XVIII may be formed from the reaction of BNO with the intermediate radical XX, which is probably produced through a proton migration from the α-$CH_3$ group of the α-MSt cation radical side in an electron-transfer complex between α-MSt and MA-$ZnCl_2$ to the MA anion radical side, according to

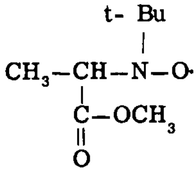


$$\text{Electron-transfer complex} \longrightarrow \underset{(XX)}{\underset{C_6H_5}{\overset{CH_2}{\overset{\|}{C}}}\text{—}CH_2\cdot} + \cdot\underset{\underset{\underset{\underset{(X\text{-}2)}{O \rightarrow ZnCl_2}}{\|}}{C\text{—}OCH_3}}{\overset{CH_3}{CH}} \quad (7)$$

$$XX + BNO \longrightarrow XVIII \quad (8)$$

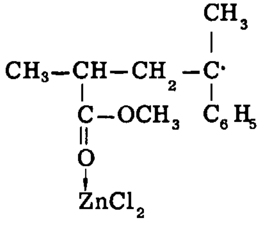
$$X\text{-}2 + BNO \longrightarrow XXI \quad (9)$$

Although the spectrum due to nitroxide XXI is not found in Fig. 9, the radical X-2 seems to react with α-MSt more easily than BNO to yield the radical XXII, which undergoes reaction with BNO to the nitroxide XIX, where R = XXII:



$CH_3-CH(C(=O)OCH_3)-N(t\text{-}Bu)-O\cdot$

(XXI)



$CH_3-CH(C(=O\rightarrow ZnCl_2)OCH_3)-CH_2-C\cdot(CH_3)(C_6H_5)$

(XXII)

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