CHEMISTRY LETTERS, pp. 273-274, 1973. Published by the Chemical Society of Japan

THE DETECTION AND IDENTIFICATION OF RADICALS PRODUCED IN THE REACTION OF N-CHLOROSUCCINIMIDE AND p-TOLUENESULFONIC ACID BY SPIN TRAPPING TECHNIQUE

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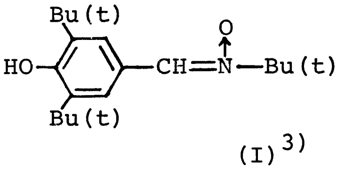
To detect and identify radical intermediates in the reaction of N-chlorosuccinimide (NCS) with p-toluenesulfonic acid (PTS), the spin trapping technique has been applied. From the reactions in the presence of some nitrones as spin trapping agent, the ESR spectrum of a nitroxide radical formed by addition of a N-succinimidyl radical to nitrone was observed.

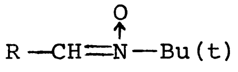
N-Halogenosuccinimides have been widely used as a halogenating agent, and the mechanism of halogenation has been investigated on the basis of a radical chain reaction by various workers. On the other hand, Dannley et al.$^{1)}$ found that N-bromosuccinimide could act as a radical initiator of vinyl polymerization via its homolysis. One of the present authors (T.O.), however, reported that N-bromosuccinimide could serve as radical initiator only in the presence of reduced nickel, and the initiating radical was the succinimidyl nitrogen radical.$^{2)}$

Recently, we also found that NCS decomposed thermally into radicals in the presence of PTS, and this system induced radical polymerization of vinyl monomers. The present letter describes on the detection and identification of radical intermediates produced in this reaction by spin trapping technique.

Spin trapping agents used in this study were α-(3,5-di-tert-butyl-4-hydroxyphenyl)-N-tert-butylnitrone (I), N-tert-butylnitrone (II) and phenyl-N-tert-butylnitrone (III), which were synthesized and purified according to the literatures.



(I)$^{3)}$

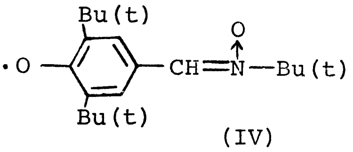


$$R-CH=\overset{\overset{O}{\uparrow}}{N}-Bu(t)$$

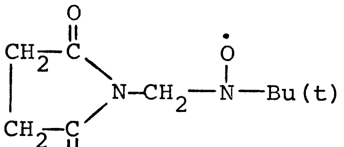
R = H (II)$^{4)}$

R = C_6H_5 (III)$^{5)}$

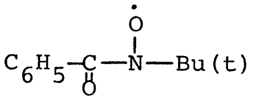
The reactions were carried out in a sealed glass ampoule in which NCS (3.74×10^{-2} mol/l), PTS (2.63×10^{-2} mol/l) and solvent ethyl acetate were placed together with the required amount of trapping agent. After a given reaction time, the ESR spectrum of the reaction mixture was recorded by a JES-ME-3X spectrometer equipped with 100 kc /sec field modulation. Spin trapping agent I has been used to characterize the radicals produced, since the carbon-radical and oxygen-radical react selectively with I to give nitroxide and phenoxy stable radicals, respectively.$^{3)}$ Fig.1 shows the ESR spectrum of the reaction mixture obtained in the presence of I. This figure shows the spectrum consisting with 18-line, and it was assigned to a phenoxy stable radical IV. This indicates that a radical other than the carbon-radical which adds to the CH=N bond of I to yield 6-line nitroxide ESR spectrum, probably succinimidyl nitrogen radical, seems to be produced in this reaction.



(IV)



(V)



(VI)

$C_6H_5\text{-}C(=O)\text{-}N(O^{\bullet})\text{-}Bu(t)$

Fig.2 shows the ESR spectrum observed in the presence of spin trapping agent II. This spectrum is assigned to nitroxide V which is produced from the reaction of succinimidyl radical with II. Although this spectrum of nitroxide V must split 27-line due to the interaction between two nitrogen atoms and two equivalent β-hydrogens, only 23-line spectrum as the result of the overlapping at the peaks indicated with arrows in Fig.2 is observed.

In order to detect other radicals than succinimidyl radical in this reaction, trapping agent III was used. In this case, the spectrum of nitroxide with no β-hydrogen and small coupling constant ($\sim$8G) of nitrogen atom is observed. It seems that of benzoyl-N-tert-butyl nitroxide (VI), because similar spectrum due to VI was also observed in the reactions of III with chlorine or di-n-butyllead dichloride.$^{5)}$ Accordingly, this finding may suggest that the chlorine atom produced in the present reaction reacts first with III to give the nitroxide VI as a final product.

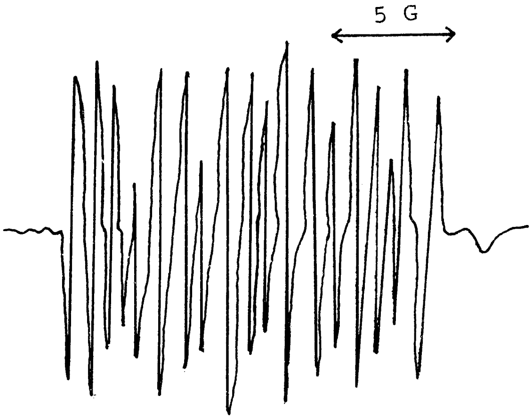


Fig.1 ESR spectrum of the reaction mixture obtained in the presence of I for 0.5 hr at 70 °C : $[I]=9.89\times10^{-2}$ mol/l

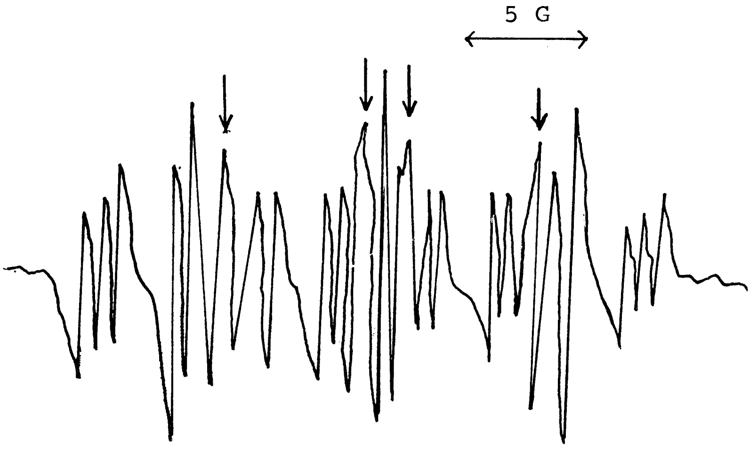


Fig.2 ESR spectrum of the reaction mixture obtained in the presence of II for 1 hr at 40 °C ; $[II]=3.24\times10^{-2}$ mol/l

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(Received November 30, 1972)