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The Behavior of Free Radicals Produced by Ultraviolet Irradiation in the Frozen Propargyl Alcohol - Hydrogen Peroxide System

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In order to assertain the polymerization mechanism in the solid state, a solid mixture of propargyl alcohol (monomer), hydrogen peroxide and water was irradiated at −196°C by an ultraviolet light. The structure of the free radicals so formed in the solid medium was then studied by the electron-spin-resonance method. The trapped free radical was a monomer radical, $CH\equiv C\text{–}\dot{C}HOH$. This shows that the HO· radicals produced by the photolysis of hydrogen peroxide abstracted the methylenic hydrogen atoms from the alcohol. An examination of the kinetic behavior of free radicals revealed that HO· radicals migrated freely and reacted with monomers at −196°C. The reaction between the monomer radical and HO· radicals is more important than the recombination between monomer radicals.

Several studies have revealed that the radiation-induced solid state polymerization proceeds by means of a free radical mechanism.[1-7] In the solid state, the usual steady-state condition of the radical concentration does not hold because of a suppressed recombination between propagation

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[1] G. Adler, D. Ballantine and B. Baysal, *J. Polymer Sci.*, **48**, 195 (1960).

[2] T. A. Fadner, I. Rubin and H. Morawetz, ibid., **37**, 549 (1959).

[3] H. Ueda and Z. Kuri, ibid., **61**, 333 (1962).

[4] T. A. Fadner and H. Morawetz, ibid., **45**, 475 (1960).

[5] H. Morawetz and T. A. Fadner, *Makromol. Chem.*, **34**, 162 (1959).

[6] H. Morawetz and I. D. Rubin, *J. Polymer Sci.*, **57**, 669 (1962).

[7] C. H. Bamford and A. D. Jenkins, ibid., **48**, 37 (1960).

radicals. Therefore, the kinetic behavior of the polymerizations is more complex than that of usual liquid state polymerizations.

In order to assertain the mechanism of radiation-induced solid state polymerizations, it may be helpful to know the behavior of free radicals in the solid state, where they are formed by a simple photolysis. So far, several electron-spin-resonance (ESR) studies have been published on photo-irradiated frozen systems of hydrogen peroxide-alcohols or vinyl monomers.[8-11] In many of the saturated and unsaturated alcohols studied, HO· radicals formed by the photolysis of hydrogen peroxide abstract α-hydrogen atoms from the alcohols.[8,9] Alcohols with triple bonds have not yet been studied in the frozen state. The reactions of a few vinyl monomers with HO· have been studied kinetically by Kuwata et al.[11] And they also studied the polymerization kinetics in detail at a temperature at which the steady state was held for the concentration of propagating radicals. However, no kinetic study has yet been made of the radical behavior at such a low temperature that the ends of the propagating radical cannot move around. In the present work, the structure of free radicals formed in the solid state of propargyl alcohol-hydrogen peroxide by photolysis at -196°C was first assigned on the basis of its ESR spectra, and then the kinetic behavior of free radicals at -196°C was examined quantitatively by varying the concentration of the monomer or of the initiator.

Experimental

Materials.—Commercial propargyl alcohol was purified by vacuum distillation. A 30% aqueous solution of hydrogen peroxide was distilled in a vacuum, and the concentrated peroxide was used for the experiment. Purified water was used as the solvent.

The Ultraviolet Irradiation of Samples.—The monomer (propargyl alcohol), hydrogen peroxide, and water were pipetted into a qualtz tube, sealed in a vacuum, and irradiated with a high pressure mercury arc (Toshiba SHL-100UV, 75Watt) for a certain length of time in a liquid nitrogen bath. The distance between the sample and the arc was about 10 cm. The irradiation conditions were the same throughout this investigation. The emission spectra of the mercury arc spread widely from 3000 Å to the visible region. The solid mixture of propargyl alcohol and a concentrated aqueous solution of hydrogen peroxide formed a transparent glass at -196°C. It could be irradiated uniformly, except for a high concentration of water, when the sample is opaque.

ESR Measurements.—The microwave frequency was 9400Mc., and the field modulation frequency was 80C. After irradiation, the sample was quickly inserted into the cavity resonator and the ESR measurements were carried out at -196°C. The concentration of free radicals was determined in comparison with that of a standard sample of a DPPH (α, α'-diphenyl-β-picryl hydrazyl) solid solution in polystyrene, the radical concentration of which had already been determined.

Results and Discussion

ESR Spectra and Their Assignment.—The ESR spectra in Fig. 1(a) were obtained with samples immediately after irradiation at -196°C. The spectra were independent of the irradiation time and the concentration of the monomer or hydrogen peroxide. Since the free radical concentration was unchanged over a long period of time at -196°C, they were completely frozen and no recombination reaction could have occurred. No ESR signal was observed when the pure hydrogen peroxide was irradiated under the same conditions. Therefore, the spectra shown in Fig. 1(a) are due to monomer radicals formed from the reaction of the monomer with the HO· radical which was produced by the photolysis of hydrogen peroxide.

The observed spectrum is a poorly-resolved triplet. It is assigned to the structure of the free radical;

$$CH{\equiv}C\text{-}\dot{C}HOH \longleftrightarrow \dot{C}H{=}C{=}CHOH$$

formed by the abstraction of one of the methylenic hydrogen atoms of a monomer molecule by HO·

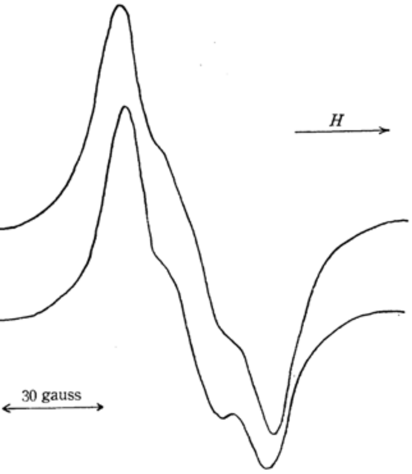

Fig. 1. ESR spectra of ultraviolet-irradiated propargyl alcohol-hydrogen peroxide glass and the effect of temperature on the spectra. (a) observed at -196°C immediately after irradiation for 4 hr. at -196°C. (b) observed at -196°C after warming at -150°C for 15 min.

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[8] J. F. Gibson, D. J. E. Ingram, M. G. R. Symons and M. G. Townsend, *Trans. Faraday Soc.*, **53**, 914 (1957).

[9] K. Kuwata, T. Ichikawa and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **83**, 652 (1962).

[10] D. J. E. Ingram, M. C. R. Symons and M. G. Townsend, *Trans. Faraday Soc.*, **54**, 409 (1958).

[11] K. Kuwata, K. Nishikida, H. Kawazura and K. Hirota, This Bulletin, **36**, 925 (1963).

radicals. Dixon et al.[12] observed the ESR spectra of the above radicals formed in the reaction between propargyl alcohol and $HO\cdot$ using a flow method. They reported the coupling constants due to each proton as $a_H(CHOH)=18.5$ gauss and $a_H(CH)=10.2$ gauss. Fessenden et al.[13] also found similar radicals by the electron-irradiation of allene:

$$CH\equiv C\text{-}\dot{C}H_2 \longleftrightarrow \dot{C}H=C=CH_2$$

These authors reported the following coupling constants: $a_H(CH)=12.6$ gauss and $a_H(CH_2)=18.9$ gauss. These spectra of the free radicals in the liquid phase showed a well-resolved hyperfine structure. However, the same type of free radicals showed poorly-resolved triplet spectra, as is shown in Fig. 1(a), since they were trapped in a rigid medium. Other possible radicals which may be formed by the reaction between the monomer and $HO\cdot$ are addition-type radicals, i.e. $H(OH)C=\dot{C}\text{-}CH_2OH$ or $\dot{C}H=C(OH)CH_2OH$. These σ-type radicals, however, may show large coupling constants.[13] Therefore, the observed spectra cannot be attributed to them.

When the temperature of the irradiated sample was raised, the concentration of free radicals decreased and the spectrum changed to that shown in Fig. 1(b). This change is caused by a new overlapping spectrum with a different *g*-value. The new spectrum is probably due to the growing polymer radicals.

The Kinetics of Free Radical Reactions.—*Experimental Results.*—The kinetic behavior of free radical reactions was studied by examining the dependence of the monomer radical ($CH\equiv C\text{-}\dot{C}HOH$) formation rate on the monomer and hydrogen peroxide concentrations at −196°C. When the hydrogen peroxide concentration, $[H_2O_2]$, was varied (the maximum $[H_2O_2]$ value was about 6 mol./l.) and the monomer concentration, [M], was kept constant, the concentration of the trapped monomer radicals, $[M\cdot]$, increased with an increase in the irradiation time, as shown in Fig. 2. (The maximum $[M\cdot]$ value was about 10^{-3} mol./l.) Figure 3 shows the initial rate of monomer radical formation, $[d[M\cdot]/dt]_{t=0}$, against $[H_2O_2]$. Apparently the rate is proportional to $[H_2O_2]$. When, in turn, $[H_2O_2]$ was kept constant and [M] was varied, (the maximum [M] was about 14 mol./l.), the $[d[M\cdot]/dt]_{t=0}$ value remained the same for all [M] values. With an increase in the irradiation time, the $d[M\cdot]/dt$ value decreased. This phenomenon cannot be ascribed to a decrease of $[H_2O_2]$ because the concentration of the trapped radicals and, consequently, the consumption of hydrogen peroxide was smaller than the initial $[H_2O_2]$.

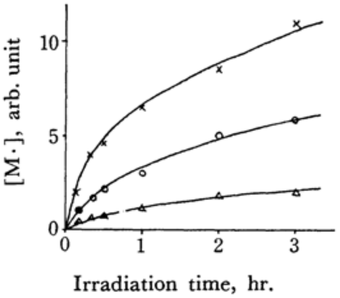

Fig. 2. The effect of irradiation time on the concentration of monomer radicals trapped in ultraviolet irradiated propargyl alcohol-H_2O_2 glass at −196°C.
[M] is kept constant.
$[H_2O_2]$: the ratio of × : ○ : △ is 5 : 3 : 1.

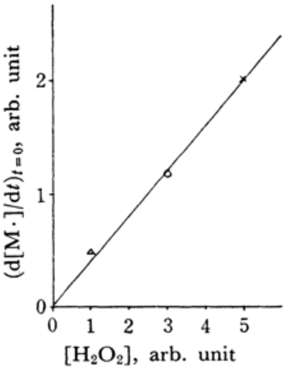

Fig. 3. The effect of hydrogen peroxide concentration on the initial rate of monomer radical formation in ultraviolet-irradiated propargyl alcohol-H_2O_2 glass at −196°C.

The Derivation of Kinetic Equations.—No ESR spectrum from $HO\cdot$ is observed after irradiation. Consequently, the $HO\cdot$ radicals formed from hydrogen peroxide during irradiation at −196°C are believed to migrate and to react readily, so that they disappear immediately after their formation. It is, therefore, reasonable to assume a steady-state $HO\cdot$ concentration in the solid state during irradiation. The experimental results indicate that monomer radicals are immobilized and that recombination between monomer radicals need not be considered. On the other hand, the concentration of monomer radicals increases to a considerable extent. This fact implies that recombination between trapped monomer radicals and the initiating $HO\cdot$ radicals should be considered as an elementary reaction, which is usually neglected in kinetic treatments of radical polymerizations in the liquid state. Consequently, the elementary reactions are as follows:

$$H_2O_2 \xrightarrow{k_1} 2HO\cdot \tag{1}$$

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[12] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, **1963**, 3119.

[13] R. W. Fessenden and R. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

$$\mathrm{HO\cdot} + \mathrm{HO\cdot} \xrightarrow{k_2} \mathrm{H_2O_2} \tag{2}$$

$$\mathrm{HO\cdot} + \mathrm{M} \xrightarrow{k_3} \mathrm{M\cdot} \tag{3}$$

$$\mathrm{HO\cdot} + \mathrm{M\cdot} \xrightarrow{k_4} \text{molecule} \tag{4}$$

From the assumption of a steady-state concentration of [HO·],

$$k_1[\mathrm{H_2O_2}] - k_2[\mathrm{HO\cdot}]^2 - k_3[\mathrm{HO\cdot}][\mathrm{M}] - k_4[\mathrm{HO\cdot}][\mathrm{M\cdot}] = 0$$

As [HO·] is small enough, one can neglect the second term. Thus, the following equation is obtained for the steady-state concentration of HO· radicals:

$$\mathrm{HO\cdot} = \frac{k_1[\mathrm{H_2O_2}]}{k_3[\mathrm{M}]+k_4[\mathrm{M\cdot}]} \tag{5}$$

From Eq. 5, the rate of monomer radical formation can be expressed as follows:

$$\frac{\mathrm{d}[\mathrm{M\cdot}]}{\mathrm{d}t} = k_3[\mathrm{HO\cdot}][\mathrm{M}] - k_4[\mathrm{HO\cdot}][\mathrm{M\cdot}] = \frac{1 - k_4[\mathrm{M\cdot}]/k_3[\mathrm{M}]}{1 + k_4[\mathrm{M\cdot}]/k_3[\mathrm{M}]}\,k_1[\mathrm{H_2O_2}] \tag{6}$$

Since $[\mathrm{M}] \gg [\mathrm{M\cdot}]$,

$$\mathrm{d}[\mathrm{M\cdot}]/\mathrm{d}t \simeq \{1 - 2k_4[\mathrm{M\cdot}]/k_3[\mathrm{M}]\}k_1[\mathrm{H_2O_2}] \tag{7}$$

By assuming that the consumption of monomer molecules and hydrogen peroxide is very small and that [M] and $[\mathrm{H_2O_2}]$ are unchanged, the integration of Eq. 7 yields:

$$[\mathrm{M\cdot}] = k_3[\mathrm{M}]/2k_4\left\{1 - \exp\left[-\frac{2k_1k_4[\mathrm{H_2O_2}]}{k_3[\mathrm{M}]}t\right]\right\} \tag{8}$$

Comparison of Experimental Results with Kinetic Equations.—The experimental results shown in Figs. 3 and 4 indicate that $\mathrm{d}[\mathrm{M\cdot}]/\mathrm{d}t \propto [\mathrm{H_2O_2}]^1[\mathrm{M}]^0$ for $t=0$. They are in good agreement with Eq.7, which shows that $\mathrm{d}[\mathrm{M\cdot}]/\mathrm{d}t = k_1[\mathrm{H_2O_2}]$ for $t=0$. From Eq. 8, [M·] is expected to show a saturating tendency with an increase in the irradiation time. In fact, this is obvious from the results shown in Figs. 2 and 4. Therefore, the two assumptions, i. e., the existence of a steady state of [HO·] and of recombination between HO· and M·, which have been made in deriving the kinetic equations, are found to be reasonable.

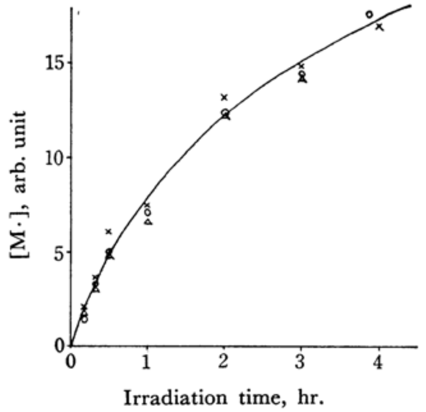

Fig. 4. The effect of irradiation time on the concentration of monomer radicals trapped in ultraviolet irradiated propargyl alcohol-$\mathrm{H_2O_2}$ glass at −196°C.
$[\mathrm{H_2O_2}]$ is kept constant.
[M]: the ratio of × : ○ : △ is 20 : 17 : 14.

From the above discussion, it may be concluded that HO· radicals migrate in the irradiated solid mixture and react readily with monomers. The reaction between the monomer radical and HO· radical is much more important than the recombination reaction between monomer radicals. This is a significant feature of the behavior of free radicals in solid state polymerization.