The Photochemical Addition Reaction. VI. The Mechanism of the Addition Reaction of n-Butyl Mercaptan to Vinyl Acetate

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Many synthetic investigations have been made on the addition reaction of mercaptans to olefins, yielding the products of β-alkylthioethyl derivatives with anti-Markownikov configuration under the influence of oxygen, peroxides and light[1]. It has been reported that, by the action of ultraviolet light, the addition of mercaptans to olefins such as vinyl acetate, vinyl chloride and allyl alcohol, proceeds according to the following overall reaction[2];

$$RSH + CH_2:CHR' \xrightarrow{h\nu} RSCH_2CH_2R' \qquad (1)$$

Recently Sivertz et al.[3] studied the kinetics of the photosensitized addition reaction of a mercaptan to various olefins in order to explain the reaction mechanism kinetically, although the identification of the reaction products was not involved in their study.

The purpose of the present study is to elucidate the mechanism of the addition reaction of mercaptans to vinyl compounds. Attention has been paid to identifying the termination product as follows: In the presence of a large excess of mercaptan, butyldisulfide has been assumed as the termination product by Sivertz et al.[3] This compound, however, has been found to decompose under ultraviolet light, which was employed for the initiation of the reaction studied. It is impossible to assume that the disulfide is the final product. Hence, the formation of the cross termination product, α, β-dibutylthioethyl derivative could not be ignored. In this connection, the analysis of all the products in the reaction has been carried out. Vinyl acetate and *n*-butyl mercaptan were chosen as the reactants, because they form 1 : 1 adduct quantitatively with no teromer formation during the reaction.

The molar ratio of vinyl acetate to mercaptan in this experiment was 1 : 20. Samples were purified by vacuum distillation for the purpose of excluding water, oxygen and oxides. The reaction mixture was irradiated with ultraviolet light of 3660 Å for forty hours. The mixture

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[1] S. O. Jones and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2452 (1938); M. S. Kharasch, W. Nudenberg and G. J. Mantell, *J. Org. Chem.*, **16**, 524 (1951).

[2] T. Hoshino, K. Yamagishi and Y. Ichikawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 510 (1953); K. Yamagishi and N. Nakajima, ibid., **75**, 1086, (1954).

[3] R. H. Pallen and C. Sivertz, *Can. J. Chem.*, **35**, 723 (1957).

irradiated was first divided into gas (fraction I) and liquid at room temperature. By the distillation of the liquid fraction at 20°C (20 mmHg) it was futher divided into two parts (named fractions II and III). One was the distillate (fraction II) consisting of excessively used mercaptan and unreacted vinyl acetate, which were collected in a cold trap (−78°C), and the other was the residue (fraction III) consisting mostly of the main product, β-butylthioethyl acetate, and the termination product, α, β-dibutylthioethyl acetate.

The mass-spectroscopic analysis of fraction I showed the mass number 2 and 88, which correspond to hydrogen and ethyl acetate, respectively. By the rectification of fraction II ethyl acetate was isolated from the mixture of unreacted vinyl acetate and excessively used mercaptan. This ethyl acetate was identified by Dragendorff's xanthate color test.[4] It is, therefore, certain that the mercaptan decomposed directly under the influence of ultraviolet light, yielding hydrogen atom and thyl radical by the primary initiation reaction of Eq. 2.

Prim. init.

$$\mathrm{RSH} \xrightarrow{h\nu} \mathrm{RS\cdot} + \mathrm{H\cdot} \qquad (2)$$

The hydrogen atom may subsequently react with vinyl acetate and mercaptan by the secondary initiation mechanisms a) and b).

a) When a hydrogen atom is added at the double bond of a vinyl acetate molecule, the acetoxyethyl radical is produced (Eq. 3) and the acetoxyethyl radical thus formed reacts with the mercaptan giving the thyl radical and the ethyl acetate (Eq. 4).

Sec. init. a)

$$\mathrm{H\cdot} + \mathrm{CH_2{:}CHOAc} \rightarrow \mathrm{CH_3\underset{\cdot}{C}HOAc} \qquad (3)$$

$$\mathrm{CH_3\underset{\cdot}{C}HOAc} + \mathrm{RSH}$$
$$\rightarrow \mathrm{RS\cdot} + \mathrm{CH_3CH_2OAc} \qquad (4)$$

b) When a hydrogen atom abstracts the hydrogen atom from a mercaptan molecule, a thyl radical and a hydrogen molecule are produced (Eq. 5).

Sec. init. b)

$$\mathrm{H\cdot} + \mathrm{RSH} \rightarrow \mathrm{RS\cdot} + \mathrm{H_2} \qquad (5)$$

In either secondary initiation a) or b), the thyl radical is produced ultimately, and the radical initiates the propagation reaction of Eqs. 6 and 7.

Prop.

$$\mathrm{RS\cdot} + \mathrm{CH_2{:}CHOAc} \rightarrow \mathrm{RSCH_2\underset{\cdot}{C}HOAc} \qquad (6)$$

$$\mathrm{RSCH_2\underset{\cdot}{C}HOAc} + \mathrm{RSH}$$
$$\rightarrow \mathrm{RS\cdot} + \mathrm{RSCH_2CH_2OAc} \qquad (7)$$

By the rectification of fraction III, the main product, β-butylthioethyl acetate was obtained in a good yield with a small amount of heavy colorless liquid (b. p. 110°C at 2 mmHg), which was identical with the authentic sample of α, β-dibutylthioethyl acetate. The identification of α, β-dibutylthioethyl acetate was performed as follows: (a) The physical properties of the sample were compared with those of the authentic sample, which was prepared by the reaction of vinyl acetate with butyldisulfide under the irradiation of ultraviolet light of 3660 Å at room temperature for forty hours (Table I). (b) α, β-Dibutylthioethyl acetate was hydrolyzed to butylthioacetaldehyde. This gave the hydrazone (m. p. 63∼64°C) with 2, 4-dinitrophenyl hydrazine and no depression of the melting point when mixed with the hydrazone of the authentic sample. The authentic sample of the aldehyde was prepared from bromacetaldehyde dimethyl acetal[8] and sodium mercaptid.

These facts indicate that β-butylthioethyl acetate is produced by the chain propagation reaction of Eqs. 6 and 7. The isolation of α, β-dibutylthioethyl acetate from the reaction mixture supports the view that termination reaction occurred by the mechanism shown in Eq. 8.

Term.

$$\mathrm{RS\cdot} + \mathrm{RSCH_2\underset{\cdot}{C}HOAc}$$
$$\rightarrow \mathrm{RSCH_2CH(SR)OAc} \qquad (8)$$

Further support of the initiation reaction was obtained by means of the experiment with oxygen as the quencher of atomic hydrogen. By the mass-spectroscopic analysis of fraction I, no ethyl acetate was identified, although traces of water and hydrogen were detected. This result suggests that the hydrogen atom combined with oxygen and the hydrogenperoxyl radical ($\mathrm{HO_2\cdot}$) thus formed produced the thyl radical and hydrogen peroxide. More thyl radicals may be produced by $\mathrm{H_2O_2}$ (Eq. 11).

$$\mathrm{H\cdot} + \mathrm{O_2} \rightarrow \mathrm{HO_2\cdot} \qquad (9)$$

$$\mathrm{HO_2\cdot} + \mathrm{RSH} \rightarrow \mathrm{RS\cdot} + \mathrm{H_2O_2} \qquad (10)$$

$$\mathrm{H_2O_2} + \mathrm{RSH} \rightarrow \mathrm{RS\cdot} + \mathrm{H_2O} \qquad (11)$$

Experimental

Materials.—*n-Butyl mercaptan.*—By the hydrolysis of *S*-butylthiuronium hydrobromide *n*-butyl mercaptan was obtained (b. p. 98°C)[5].

Vinyl acetate.—After removing the impurities in a commercial product by Matheson's prepolymerization method[6], the remaining monomer was

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4) F. Feigl, "Spot Tests in Organic Analysis", Elsevier Publ. Co., Amsterdam (1956), p. 174.

5) H. Backer, *Rec. trav. chim.*, **51**, 289 (1932).

6) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 2610 (1949).

TABLE I.

α, β-Dibutylthioethyl acetate	Boiling point °C at mmHg	Refractive index n_D	Anal. Found C	H
The sample from reaction products	107/0.3	1.4958 (20°C)	54.58	9.29
The authentic sample	109/0.3	1.4948 (24°C)	54.22	9.25
Calcd. for $C_{12}H_{24}O_2S_2$:			54.53	9.15

fractionated and the fraction of b. p. 72.6°C was collected and the sample was stored in vacuo.

The purification of these two samples was effected at first by fractional distillation under nitrogen through a Steadmann type of glass column with 100 plates and the distillate was further purified of a high vacuum system. The out gassing of the liquid sample in the vacuum distillation was achieved by repeated freezing and pumping until no more non-condensible gas was evolved. The liquid sample in the system was then distilled into a vacuum reactor.

The purity of the vinyl acetate was checked by measuring the absorption spectrum. The original crude sample showed two bands at 2680 and 2590 Å, in which the band at 2590 Å was decided to be due to the acetaldehyde present in the sample. These impurity bands were completely removed by the purification described above and no band appeared between 2500 and 3000 Å in the spectrum of the purified sample. The purified sample showed no induction period in the polymerization initiated by 2, 2′-azo-bis-*iso*-butyronitrile in the concentration of 10^{-4} mol. per liter. This is also an indication of the high purity of the sample.

Apparatus. — The parallel light from a Gleiter high pressure mercury lamp (SHL-200 W.) with a condenser was filtered with a Matsuda-UVD2 filter to obtain monochromatic light of 3660 Å. The intensity of the light was measured by a photoelectric tube and was kept constant by controlling the current through the lamp. The mass spectra were observed by a modified Hitachi RMA mass spectrometer. For the study of absorption spectra, a Beckman DU Spectrophotometer was used with 1 cm. cells.

Procedure.—The purified vinyl acetate (5.83 g.) and *n*-butyl mercaptan (122 g.) were measured in calibrated tubes and were mixed in a reaction cell in the molecular ratio of olefin to mercaptan 1 : 20.

The reaction cell with a reaction mixture was sealed off from the vacuum line and was irradiated with ultraviolet light of 3660 Å for forty hours. The irradiated mixture which was collected from three reaction cells, was first divided into gas (fraction I) and liquid at room temperature. By the distillation of the liquid fraction at 20°C (20 mmHg), it was further divided into two parts (named fractions II and III). One was the distillate (fraction II) consisting of excessively used mercaptan and unreacted vinyl acetate, which were collected in a cold trap (−78°C), and the other was residue (fraction III), consisting mostly of the main product, β-butylthioethyl acetate, and the termination product, α, β-dibutylthioethyl acetate.

The mass-spectroscopic analysis of fraction I showed the mass numbers 2 and 88, which correspond to hydrogen and ethyl acetate, respectively.

Fraction II was distilled fractionally with a Steadmann type glass column at an atmospheric pressure under nitrogen. One gram of crude ethyl acetate (b. p. 78.1∼83.0°C) and 0.5 g. of unreacted vinyl acetate (b. p. 72.1∼73.0°C) were obtained together with mercaptan. In order to confirm the existence of ethyl acetate, Dragendorff's xanthate color test[4] was carried out on the crude fraction (b. p. 78.1∼83.0°C). The test showed violet color, the indication of ethoxyl residue. The same color test gave us no color with vinyl acetate and blue color with mercaptan.

Fraction III was fractionated under reduced pressure. Thirty-two grams of β-butylthioethyl acetate (b. p. 62°C at 0.7 mmHg n_D^{25} 1.4954) was obtained as the main product. Another product of α, β-dibutylthioethyl acetate (0.3 g.) was identified as follows.

(a) The physical properties of the sample were compared with those of the authentic sample (Table I). The authentic sample was prepared in 30% yield by the reaction of vinyl acetate (0.1 mol.) with butyldisulfide[7] (0.5 mol.) under the irradiation of ultraviolet light of 3660 Å at room temperature for forty hours.

(b) α, β-Dibutylthioethyl acetate was hydrolyzed to butylthioacetaldehyde by steam distillation with a drop of sulfuric acid. The aldehyde gave a hydrazone (m.p. 63∼64°C) with 2, 4-dinitrophenyl hydrazine and no depression of the melting point when mixed with the hydrazone of the authentic sample. The authentic sample was prepared as follows: The solution of sodium mercaptid (0.5 mol.) in ethanol (200 ml.) was added to the solution of bromoacetaldehyde dimethyl acetal[8] (0.5 mol.) in ethanol (30 ml.) at room temperature. After refluxing for half an hour, sodium bromide and ethanol were removed and *n*-butylthioacetaldehyde diethyl acetal (b. p. 75°C at 0.1 mmHg, n_D^{25} 1.4532) was obtained in the yield of 60.0%.

Found: C, 54.02; H, 10.43. Calcd. for $C_8H_{18}O_2S$: C, 53.91; H, 10.18%.

n-Butylthioacetaldehyde dimethylacetal was hydrolyzed by refluxing with dilute sulfuric acid. *n*-Butylthioacetaldehyde (b. p. 88°C at 24 mmHg) was obtained from the reaction mixture by steam distillation in the yield of 77.6%. The 2, 4-dinitrophenyl hydrazone of this substance had m. p. 62.0∼63.0°C.

Found: N, 17.53. Calcd. for $C_{12}H_{16}O_4N_4S$: N, 17.94%.

When oxygen was used as the quencher of atomic hydrogen the reaction mixture was exposed to dry air in the reaction cell before the irradiation and

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[7] L. D. Small, J. H. Bailey and C. J. Cavallito, ibid., **69**, 1711 (1947).

[8] P. Z. Bedoukian, ibid., **66**, 651 (1944).

the cell was sealed off from the vacuum line at -78°C. By the analysis of fraction I no ethyl acetate was identified, although traces of water and hydrogen were detected.

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