The Radiation-induced cis-trans Isomerization of 2-Butenes by Hydrogen Sulfide*

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The radiation-induced free radical addition of hydrogen sulfide to olefins is a reaction which has been often studied;[1-4] it is considered to involve the following chain propagating steps:

$$H_2S \xrightarrow{\gamma} HS\cdot + H \tag{1}$$

$$HS\cdot + CH_2{=}CHR \rightarrow HS\dot{C}H_2{-}CHR \tag{2}$$

$$HSCH_2{-}\dot{C}HR + H_2S \rightarrow HSCH_2{-}CH_2R + HS\cdot \tag{3}$$

The thiols, once formed, undergo further reaction with olefins to give the corresponding sulfides. The free radical addition of thiols to olefins is considered to involve the following similar chain-propagating steps:[5,6]

$$RCH_2CH_2SH \xrightarrow{\gamma} RCH_2{-}CH_2S\cdot + H \tag{4}$$

$$RCH_2{-}CH_2S\cdot + CH_2{=}CHR \rightarrow RCH_2{-}CH_2SCH_2{-}\dot{C}HR \tag{5}$$

$$RCH_2{-}CH_2SCH_2{-}\dot{C}HR + RCH_2{-}CH_2SH \rightarrow (RCH_2{-}CH_2)_2S + RCH_2{-}CH_2S\cdot \tag{6}$$

In a previous paper[7] of this series, evidence was presented for the abstraction of hydrogen atoms from hydrocarbons either by sulfhydryl radicals or thiyl radicals; that is, the reactions which are essentially the reverse of 3 and 6 can occur with ease in certain systems. There is also good reason to believe that reactions 2 and 5 may be reversible as well, in view of several previous works on similar thiol-addition reactions to olefins.[7,8] In studying the addition of methanethiol to isobutene, propylene and ethylene in the gas phase, Sivertz et al.[9] have found negative overall activation energies of 8 to 9 kcal. The photoisomerization of *cis*- and *trans*-2-butenes in the presence of methanethiol has also been studied recently.[10] Especially interesting is the work by Skell and Allen, who demonstrated that the orientation of the free radical addition of CH_3SD is controlled by the strength of the deuterium-bound bond.[11] Meanwhile, experiments in our work[2] have demonstrated the reversibility of the radical-addition reaction in the gas-phase mixtures of hydrogen sulfide and olefins by the rapid isomerization of unreacted olefin during the irradiations at room temperature. This paper will present more detailed data on this reversibility.

Experimental

Irradiations.—The gamma radiation was provided either by a 100-curie or a 1000-curie cobalt-60 source.[12] The dose rates were obtained from the Fricke ferrous sulfate dosimeter, taking G as 15.6,[13] and from the Victoreen rate meter. The G-values were calculated from the relation of the products formed and the absorption energy of the gaseous sample. The absorption energies of 2-butenes and of hydrogen sulfide were corrected in electron density from the absorption of air, 83.8 erg./g./r.; 2-butenes correspond to 95.7 erg./g./r., and hydrogen sulfide, to 88.7 erg./g./r. All the irradiations were carried out at room temperature.

Reaction Vessel.—The irradiation vessel used for these gaseous reactions was a Pyrex tube 25 mm. in outside diameter and 20 cm. long and equipped with a breakoff seal.

Materials.—*cis*-2-Butene and *trans*-2-butene were purchased from the Takachiho Chemicals Co., Tokyo, and hydrogen sulfide, from Seitetsu Chemicals Co., Kakogawa; both were purified by fractional distillations. The impurities in both the 2-butenes and the hydrogen sulfide used were found to be less than 0.5% by gas chromatographic analysis.

Analyses.—Conventional high-vacuum techniques

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* The Study of the Radiation Chemistry of Organic Sulfur Compounds. Part VIII.

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were employed throughout the investigation. All the analyses of the irradiated samples were carried out by a combination of fractional distillation and gas chromatographic separation.

The irradiated sample was passed first through a series of dry ice - acetone cooled traps, then through carbon disulfide - cooled traps, and finally through liquid nitrogen traps. The fraction condensed in dry ice - acetone cooled traps was found to be a mixture of 2-butanethiol and di-2-butyl sulfide. The condensed gas at the carbon disulfide - cooled traps was identified as a mixture of unreacted and isomerized 2-butene. This portion was measured by gas chromatography (Hitachi type KGL-2A), using a 90 m. Golay column coated with squalane and operated at room temperature with a He carrier at 1.5 kg./cm². The condensed gas at liquid nitrogen was identified as unreacted hydrogen sulfide.

Results and Discussion

Samples of mixtures consisting of various amounts of pure *trans*-2-butene and hydrogen sulfide were irradiated in a static system as has been described in the "Experimental" section. These were then periodically analyzed by gas chromatography. The results of such experiments are shown in Table I. The isomerized mixtures show the compositions of 72% and 28% for *trans*- and *cis*-2-butenes respectively. Similar experiments carried out on pure *cis*-2-butene gave the results shown in Table I. Here again, the values obtained for trans-cis are nearly identical, i. e., 73%-27%. The radiation-induced equilibrium of *trans*- and *cis*-butenes by hydrogen sulfide obtained under various conditions are shown in Table I; the cis-trans isomerization readily reaches an equilibrium and gives a mixture of 28% and 72% of *cis*- and *trans*-2-butenes. Meanwhile, the *G*-value of 2-butanethiol formation was found to be about $4-9\times10^3$, and the rate was shown to be linear to the square root of the dose rate.

To determine the yield of the radiation-induced cis-trans isomerization in somewhat more detail, mixtures of various amounts of *cis*-2-butene and hydrogen sulfide were subjected to small doses of irradiation. The results of these experiments are shown in Fig. 1. Within these irradiation doses, the amount of trans-isomerization is proportional to the energy absorbed, and no thiol and sulfide were detected among the products.

TABLE I. THE RADIATION-INDUCED ISOMERIZATION OF *cis*- AND *trans*-2-BUTENE BY HYDROGEN SULFIDE

Dose rate r./hr.	*trans*-Butene* 24 hr.	*trans*-Butene* 48 hr.	*cis*-Butene* 48 hr.
2.8×10^4	trans 72% cis 28%	trans 72% cis 28%	trans 73% cis 27%
1.1×10^4		trans 72% cis 29%	trans 73% cis 27%
5.7×10^3		trans 71% cis 29%	

* Composition of reaction mixtures: 2-butenes, 1140 mmHg; H_2S, 670 mmHg

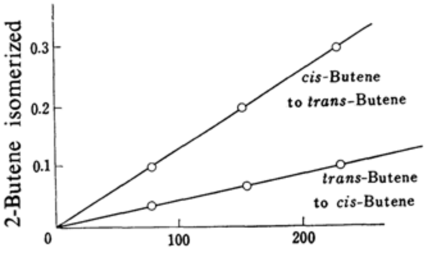
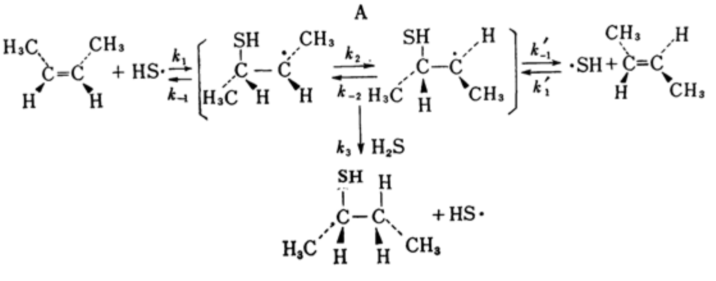


Fig. 1. The radiation-induced isomerization of *trans*- and *cis*-2-butene with hydrogen sulfide. (Sample: 2-butene 2.48 mmol., H_2S 0.90 mmol.)

The radiation-induced isomerizations of *cis*-2-butene alone, without any addent, namely direct isomerizations, were also performed. The *G*-value of the direct isomerization is 300, while the *G*-value of the isomerization by sulfhydryl radicals was found to be around 2.5×10^5. These results can be well explained by the formation of intermediate radicals (A) by the attack of the sulfhydryl radical on 2-butene.

If one assumes that the initial step of the reaction is the attack of the sulfhydryl radical on 2-butene, one can write the scheme for the reaction as in 7, where k_3, the rate of hydrogen abstraction, is much smaller than k_2 or k_{-2}, the rate of the equilibration of the incipient radical A.



(7)

The intermediate incipient radical presumably readily regenerates the equibrium mixture of *cis*- and *trans*-2-butenes by losing the sulfhydryl radical.

Since the reaction of sulfhydryl radicals with 2-butenes to form the incipient radical A is presumed to be reversible, the trans isomer appears in the unreacted 2-butene in the addition reaction of hydrogen sulfide to *cis*-2-butene by gamma irradiations. It was found that the *G*-value for the formation of *trans*-2-butene from the composite radical was 50 times that of the formation of the addition product by the hydrogen transfer from hydrogen sulfide. The *G*-value for *cis*-2-butene formation is 20 times that for the formation of the addition product. Therefore, the decomposition of the incipient radical into the sulfhydryl radical and 2-butenes is very rapid compared to the hydrogen transfer reaction with hydrogen sulfide.

In this respect, the γ-ray induced isomerization of 2-butenes by H_2S is essentially the same as that by photochemical isomerization with methanethiol,(10) and it involves the reversible formation of an incipient radical intermediate, as has been described in Eq. 2. The larger *G*-value of the isomerization from *cis*-2-butene than that from the trans isomer seems to suggest that the initial addition and the final loss of the sulfhydryl radical are very fast and that the rate is controlled by the rotation barrier in A. Meanwhile, the rate-determining step in the formation of the addition product is thought to be 3, the activation energy for which is estimated to lie between 2 and 3 kcal.(14)

Summary

Radiation-induced free radical isomerizations of 2-butenes with hydrogen sulfide at room temperature gave identical mixtures of about 72% *trans*- and 28% *cis*-butenes. The *G*-value of the isomerization is 20 to 50 times larger than that of the formation of the addition product. With gamma irradiation, 2-butenes in the presence of hydrogen sulfide were rapidly isomerized, even with a very small radiation dose. This ready isomerization indicates the ease of the reversibility of the first step of the sulfhydryl-radical addition reactions.

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