The Radiation-induced Addition of Hydrogen Sulfide to Olefins*

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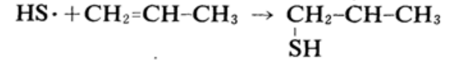
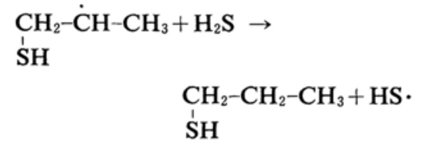
In a previous investigation of the radiation-induced addition of hydrogen sulfide to propylene,[1] the formation of *n*-propyl mercaptan and of di-*n*-propyl sulfide have been observed. The radiation-induced addition of hydrogen sulfide to propylene took place very readily, and was completed at room temperature with a relatively small radiation dose. The *G*-values of this reaction were found to be more than ten thousand, while the addition followed the anti-Markownikov rule. Apparently the reaction proceeds through a free radical chain process, where the sulfhydryl radicals formed in the initial step of the radiolysis of hydrogen sulfide undergo a radical addition to the propylene in the following chain propagating step:

$$H_2S \rightsquigarrow HS\cdot + \cdot H \qquad (1)$$



$$HS\cdot + CH_2{=}CH{-}CH_3 \rightarrow \underset{\displaystyle SH}{CH_2}{-}\dot{C}H{-}CH_3 \qquad (2)$$



$$\underset{\displaystyle SH}{CH_2}{-}\dot{C}H{-}CH_3 + H_2S \rightarrow \underset{\displaystyle SH}{CH_2}{-}CH_2{-}CH_3 + HS\cdot \qquad (3)$$

In the present work, the radiation-induced addition of hydrogen sulfide to propylene has been extended to other various gaseous olefins.

Experimental

Irradiations.—The gamma radiation was provided by a 1000-curie or a 5000-curie cobalt-60 source.[2] Samples were irradiated at fixed positions at which the dose rates were 1.9×10^5, 2.8×10^4, 1.1×10^4, and 5.7×10^3 r./hr. respectively. The dose rates were obtained by means of a Fricke ferrous sulfate dosimeter, taking *G* as 15.6.[3]

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

Materials.—All the olefins except butadiene were purchased from the Takachiho Chemicals Co., Tokyo, and hydrogen sulfide, from the Seitetsu Chemicals Co., Kakogawa; both were purified by vacuum distillations. Butadiene was obtained from the Japan Synthetic Rubber Co., Yokkaichi. The impurities in both the olefins and hydrogen sulfide used were found to be less than 0.5% by gas chromatographic analysis.

Analysis.—Conventional high-vacuum techniques 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.

Isobutene with Hydrogen Sulfide. — The samples were analyzed by the same procedure as was used in the case of propylene.[1]

cis- and trans-2-Butene with Hydrogen Sulfide.—The procedure will be explained in the following paper.[4]

Various Olefins with Hydrogen Sulfide. — The irradiated samples were first passed through a series of dry ice - acetone cooled traps and then through a liquid nitrogen - cooled trap. The fraction condensed in the dry ice - acetone cooled trap was analyzed qualitatively by a gas chromatograph (Hitachi type KGL-2A), using a 90 m. Golay column coated with squalane. The amount of thiols in this fraction was determined by potentiometric titration with silver nitrate in isopropyl alcohol.[5]

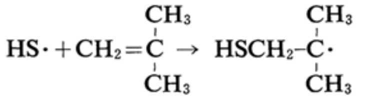
Results and Discussion

Various amounts of olefins were mixed with hydrogen sulfide, and these mixtures were irradiated at several radiation doses in static systems.

The Radiation-induced Addition of Hydrogen Sulfide to Isobutene.—The mixtures of hydrogen sulfide and isobutene were irradiated with cobalt-60 gamma rays; these results are shown in Table I. The addition is undoubtedly initiated by the decomposition of hydrogen sulfide, as is shown by:

$$H_2S \xrightarrow{\gamma} HS\cdot + \cdot H \qquad (1)$$

Then the sulfhydryl radical thus formed attacks isobutene:



$$HS\cdot + CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} \rightarrow HSCH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}\cdot \qquad (4)$$

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* The Study of the Radiation Chemistry of Organic Sulfur Compounds. Part VII. Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

1) K. Sugimoto, W. Ando and S. Oae, This Bulletin, **37**, 365 (1964).

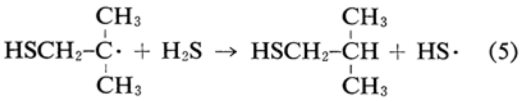
2) T. Azuma et al., *Ann. Rept. Radiation Center Osaka Pref.*, **2**, 56 (1961).

3) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

4) K. Sugimoto, W. Ando and S. Oae, This Bulletin, **38**, 224 (1965).

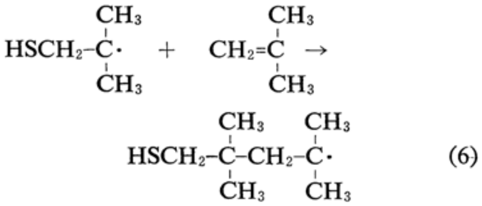
5) M. W. Tamele and L. B. Ryland, *Ind. Eng. Chem., Anal. Ed.*, **8**, 16 (1936).

The adduct radical formed can react with hydrogen sulfide, yielding 2-methylpropylmercaptan:



$$\mathrm{HSCH_2{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot + H_2S \rightarrow HSCH_2{-}\overset{CH_3}{\underset{CH_3}{C}}H + HS\cdot} \qquad (5)$$

or with isobutene, giving the propagating radical:



$$\mathrm{HSCH_2{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot \;+\; CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} \rightarrow HSCH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot} \qquad (6)$$

Steps 4 and 5 are the chain-carrying steps of the addition of hydrogen sulfide to isobutene, while step 6 is the propagating step of telomer production. The experiments indicate that reaction 5 proceeds in preference to reaction 6.

TABLE I. THE RESULTS OF THE RADIATION-INDUCED ADDITION OF HYDROGEN SULFIDE TO ISOBUTENE

Dose rate r./hr.	Product	Amount of product mmol.	
		Irrd. time 24 hr.	Irrd. time 48 hr.
2.8×10^4	2-Methylpropylmercaptan	1.53(24%)	1.35(21%)
	Di(2-methylpropyl) sulfide	1.88(59%)	2.47(78%)
1.1×10^4	2-Methylpropylmercaptan		1.53(29%)
	Di(2-methylpropyl) sulfide		2.22(70%)
5.7×10^3	2-Methylpropylmercaptan		1.26(20%)
	Di(2-methylpropyl) sulfide		1.68(53%)

Sample: Isobutene, 980 mmHg, 6.33 mmol.; H_2S, 700 mmHg, 4.50 mmol.

The telomer was not found in the products. The reactivity of isobutene with hydrogen sulfide is nearly equal to that of propylene with hydrogen sulfide, while that of *trans* or *cis*-2-butene with hydrogen sulfide is one-tenth of that of propylene or isobutene, as shown in Tables II and III. The difference between these reactivities might depend on the reactivity of each olefin. The radiation-indcued polymerization of isobutene did take place and was easy to follow, while no polymerizations of *cis*- and *trans*-2-butenes were recognized. Under the conditions of cationic polymerization,⁶⁾ at room temperature, isobutene has been shown to polymerize much more readily than 2-butenes.

The Radiation-induced Addition of Hydrogen Sulfide to *trans*- or *cis*-2-Butene.—The results of the radiation-induced addition of hydrogen sulfide to 2-butenes are shown in Tables II and III. In the addition reaction of *trans*- or *cis*-2-butene, a rapid isomerization of 2-butene was found to take pleace simultaneously; hence, in Table II the amounts of *cis*-2-butene isomerized from *trans*-2-butene are also shown. The radiation-induced equilibriation of *trans*- and *cis*-2-butene with hydrogen sulfide is readily, attained. The cis-trans ratio reaches a limiting value, 28 to 72, under various conditions. On the other hand, the *G*-values of the 1-methylpropylmercaptan formed are $4-9\times10^3$, and the rate of reaction has been shown to be linear to the square root of the dose rate.

The Formation of Thiols by the Radiation-induced Reaction of Hydrogen Sulfide with Olefins.—When one wants to obtain thiols, it is desirable to employ a large excess of hydrogen sulfide, or to separate the thiols at an early stage of the radiation-induced reaction.¹⁾ Thiols were the only products obtained when the amount of hydrogen sulfide added was 6—8 times more than that of an unsaturated compound in this radiation-induced addition

TABLE II. THE RESULTS OF THE RADIATION-INDUCED ADDITION OF HYDROGEN SULFIDE TO *trans*-2-BUTENE

Does rate, r./hr.	Product	*G*-value	Amount of product, mmol.	
			Irrd. time 24 hr.	Irrd. time 48 hr.
2.8×10^4	1-Methylpropylmercaptan	4.1×10^3	0.18 (2.6%)	0.26 (3.7%)
	cis-2-Butene		1.67 (24%)	1.60 (23%)
1.1×10^4	1-Methylpropylmercaptan	7.1×10^3	0.15 (2.2%)	0.23 (3.3%)
	cis-2-Butene			1.60 (23%)
5.7×10^3	1-Methylpropylmercaptan	8.5×10^3		0.18 (2.6%)
	cis-2-Butene			1.74 (25%)

Sample: *trans*-2-Butene, 6.95 mmol.; H_2S, 4.10 mmol.

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6) W. H. T. Davison, S. H. Piwner and R. Worrall, *Proc. Roy. Soc.*, **A252**, 187 (1959).

TABLE III. THE RESULTS OF THE RADIATION-INDUCED ADDITION OF HYDROGEN SULFIDE TO *cis*-2-BUTENE

Dose rate r./hr.	Product	Amount of product, mmol. Irrd. time 24 hr.
	1-Methylpropylmercaptan	0.19 (2.7%)
2.8×10^4	Di(1-methylpropyl)sulfide	0.50 (14%)
	trans-2-Butene	4.17 (60%)
	1-Methylpropylmercaptan	0.17 (2.4%)
1.1×10^4	Di(1-methylpropyl)sulfide	0.49 (14%)
	trans-2-Butene	4.31 (62%)
	1-Methylpropylmercaptan	0.20 (2.9%)
5.7×10^3	Di(1-methylpropyl)sulfide	
	trans-2-Butene	

Sample: *cis*-2-Butene, 6.95 mmol.;
H_2S, 4.10 mmol.

TABLE IV. THE FORMATION OF THIOLS BY THE RADIATION-INDUCED REACTION OF HYDROGEN SULFIDE TO OLEFINS

Olefin	Amount of thiol formed, mmol.
Ethylene	1.45
Propylene	1.40
1-Butene	0.94
Isobutene	0.75
cis-2-Butene	0.52
trans-2-Butene	0.50
Butadiene	0.00
Acetylene	0.18

Dose rate: 1.9×10^5 r./hr. Radiation dose: 5.7×10^5 r.
Sample: Olefin, 2.15 mmol.;
H_2S, 12.6 mmol.

reaction. Here, the addition follows the anti-Markownikov rule. The experiment of the addition of hydrogen sulfide has been extended to various olefins; the results of the radiation-induced addition are listed in Table IV.

Apparently the reactivities of various olefins toward hydrogen sulfide are different in this addition reaction, and the radical chain of these reactions seems to decrease with an increase in the carbon number of olefins. However, all the olefins apparently underwent a similar radical chain process, and the *G*-value dependence of dose rate is also similar to the case of propylene with hydrogen sulfide.(1)

The radiation-induced addition of hydrogen sulfide to butadiene was not observed. The addition of hydrogen sulfide to butadiene was substantially more difficult than that to other olefins. Similar phenomena have been reported by Sivertz(7) in the photo-initiated addition of methyl mercaptan. The photo-initiated addition of methyl mercaptan to isobutene, ethylene and butadiene in the gas phase has yielded overall negative activation energies of −8900, −8800, −7900 and +2800 respectively. The rate-determining step is thought to be hydrogn abstraction, for which the activation energy is estimated to lie between 2 and 3 kcal. for all except butadiene, which is considerably higher, about 6 kcal.

Summary

The radiation-induced free radical addition of hydrogen sulfide to olefins to give the corresponding thiols has been studied. The addition of the thiols to olefins has been found to undergo a free radical chain reaction, readily yielding the corresponding sulfides in the succeeding step. However, the thiols were found to be the only component when an excess of hydrogen sulfide was used. The reactivity of the radical chain reaction decreases with an increase in the carbon number of α-olefins.

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7) C. Sivertz, W. Andrews, W. Elsdon and K. Grabam, *J. Polymer Sci.*, **19**, 587 (1956).