*The Radiation-induced Addition of Hydrogen Sulfide to Propylene**

By Ken'ichi SUGIMOTO, Wataru ANDO and Shigeru OAE

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The free-radical addition of thiols to olefinic compounds has been studied extensively during the past twenty-five years,⁽¹⁾ but the addition of hydrogen sulfide to olefinic compounds has received rather scanty attention. The photochemical addition of hydrogen sulfide to olefinic bonds has, however, at least been shown to give mixtures of the corresponding mercaptans and the sulfides.⁽²⁾ This paper will present the results of a study of the gamma-ray initiated free radical addition of hydrogen sulfide to propylene.

The radiation-induced addition of hydrogen sulfide to propylene took place very readily, giving mainly *n*-propylmercaptan and di-*n*-propylsulfide, 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. The addition followed a non-Markownikoff rule, as in the case of the change of mercaptan to olefins.⁽³⁾ 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 olefin in the following chain-propagating step.

During the preparation of this paper, a report⁽⁴⁾ on the X-ray initiated addition of hydrogen sulfide to fluoroethylenes appeared. Although the *G*-values for these reactions were somewhat smaller than those of the present work, the nature of the addition appears to be similar.

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1) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y. (1957), p. 313.

2) W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **7**. 472 (1942).

3) Posner, *Ber.*, **38**, 646 (1905).

4) J. F. Harris, Jr. and F. W. Stacey, *J. Am. Chem. Soc.*, **85**, 749 (1963).

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

			Amount of product, mmol.			
Dose rate r/hr.	Product	Net G-value	Irradiation time 24 hr.	Irradiation time 48 hr.		
					Apparent yield	Net yield
2.8×10^4	C_3H_7SH	2.5×10^4	1.30	1.48	20%	83%
	$(C_3H_7)_2S$	1.1×10^4	1.93	2.34	63%	63%
1.1×10^4	C_3H_7SH	3.6×10^4	1.50	1.40	19%	71%
	$(C_3H_7)_2S$	1.7×10^4	1.31	1.96	52%	52%
5.7×10^3	C_3H_7SH	5.6×10^4	1.08	1.43	19%	62%
	$(C_3H_7)_2S$	2.6×10^4	1.12	1.59	43%	43%

Sample	C_3H_6	1160 mmHg	7.48 mmol.
	H_2S	660 mmHg	4.27 mmol.

TABLE II. THE AMOUNTS OF PRODUCTS AND THE YIELD FOR INITIAL AMOUNT OF PROPYLENE

Component	Product	24 hr.	48 hr.	96 hr.
7.48 mmol. C_3H_6	C_3H_7SH	2.12 mmol. (28%)	2.04 mmol. (27%)	
6.41 mmol. H_2S	$(C_3H_7)_2S$	1.49 mmol. (40%)	2.41 mmol. (64%)	
7.48 mmol. C_3H_6	C_3H_7SH	1.50 mmol. (20%)	1.40 mmol. (19%)	0.88 mmol. (12%)
4.27 mmol. H_2S	$(C_3H_7)_2S$	1.31 mmol. (35%)	1.96 mmol. (52%)	2.67 mmol. (71%)
7.48 mmol. C_3H_6	C_3H_7SH	0.73 mmol. (10%)	0.86 mmol. (11%)	
2.59 mmol. H_2S	$(C_3H_7)_2S$	0.72 mmol. (19%)	1.08 mmol. (29%)	

Irradiation dose rate 1.1×10^4 r/hr.

Experimental

Irradiations.—The gamma radiation was provided by a 1000 curie cobalt-60 source.[5] The dose rates were obtained by means of a Fricke ferrous sulfate dosimeter, taking G as 15.6.[6] Samples were irradiated at three fixed positions, at which the dose rates were 2.8×10^4, 1.1×10^4, and 5.7×10^3 r/hr. respectively. The G-values were calculated from the relation of the products formed and the absorption energy of the gaseous sample. The absorption energies of propylene and hydrogen sulfide were based on the absorption energy of air, 88 erg./g./r. All the irradiations were carried out at room temperature.

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

Materials.—Propylene was purchased from the Takachiho Chemicals Co., Tokyo, and hydrogen sulfide, from the Seitetsu Chemicals Co., Kakogawa; both were purified by vacuum distillation. The impurities in both the propylene and the hydrogen sulfide used were found to be less than 0.5% by gas-chromatographic analysis.

Analyses.—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. The irradiated sample was passed first through a series of dry-ice acetone-cooled traps and then through liquid nitrogen-cooled traps.

The fraction condensed in dry-ice acetone cooled traps was analyzed by gas-chromatography (Hitachi Type KGL-2A) using a 2 m. column packed with celite 545, impregnated with 30% silicon DC 550 and operated at 80°C with an H_2 carrier at 40 ml./min.; it was found to be a mixture of *n*-propylmercaptan and di-*n*-propylsulfide. The amount of *n*-propylmercaptan was also determined by potentiometric titration with silver nitrate in isopropyl alcohol;[7] the end point was found to be between approximately −200 and −50 mV. vs. SCE. On the other hand, the amount of di-*n*-propylsulfide was calculated by subtracting that of the *n*-propylmercaptan formed from the amounts of hydrogen sulfide and propylene reacted. The gas which condensed at the liquid-nitrogen temperature through a series of dry-ice acetone traps was identified as unreacted hydrogen sulfide and propylene. This portion was measured by a manometer.

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[5] T. Azuma et al., *Ann. Rept. Rad. Center, Osaka Pref.*, **2**, 56 (1961).

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

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

Results and Discussion

Various amounts of hydrogen sulfide were mixed with propylene, and these mixtures were irradiated at several radiation doses in a static system. The results of the radiation-induced addition of hydrogen sulfide to propylene are shown in Tables I and II.

In Table I, the apparent yield of products means the amount of the final products formed against the initial amount of propylene, while the net yield is the total amount of *n*-propylmercaptan formed during the reaction, that is, the actual amount of the mercaptan plus the sulfide formed, because the *n*-propylmercaptan is gradually converted to the di-*n*-propylsulfide by the further reaction of *n*-propylmercaptan with propylene.

The Effects of the Dose Rate on the *G*-Value.—The effects of dose rate *I* on the yield are shown in Figs. 1 and 2. The *G*-values were estimated from the initial inclination of the curves in Fig. 1, while the logarithms of the *G*-values are plotted against the logarithms of *I* in Fig. 2. From these plots, it is clearly shown that *n*-propylmercaptan and di-*n*-propylsulfide are produced in proportion to the -0.52 and -0.54 powers of *I*. These values are slightly smaller than -0.50 which would be derived under the assumption of a bimolecular termination of all the propagating radicals. This finding also seems to indicate a radical chain mechanism[8] for this radiation-induced reaction.

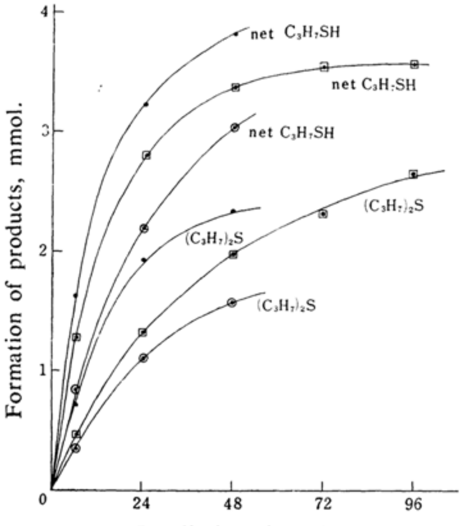

Fig. 1. The formations of *n*-propylmercaptan and di-*n*-propylsulfide.
• 2.8×10^4 r/hr. ▣ 1.1×10^4 r/hr.
⊙ 5.7×10^3 r/hr.
Sample C_3H_6 7.48 mmol.
H_2S 4.27 mmol.

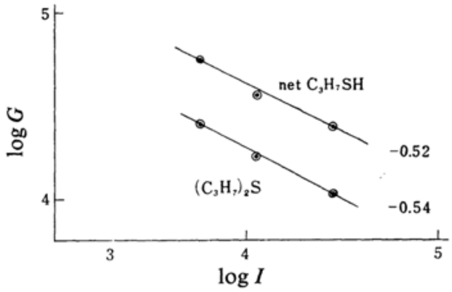

Fig. 2. The relation of log *G* and log *I*.

The Effect of the Molar Ratio of the Hydrogen Sulfide in the Sample.—It is shown in Fig. 3 that the yield increases with the increasing molar ratio of hydrogen sulfide, while the inclination of the curve gradually decreases. It would be interesting to see whether or not the yield will keep increasing at a higher molar per cent of hydrogen sulfide. Further work in this connection is in progress in our laboratory.

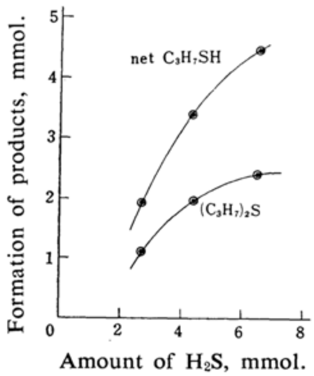

Fig. 3. Effect of molar ratio of hydrogen sulfide in the sample.
Dose rate 1.1×10^4 r/hr.
Irradiation time 48 hr.
C_3H_6 7.48 mmol.

When one makes *n*-propylmercaptan, it is desirable to employ a large molar ratio of hydrogen sulfide initially, or to separate the mercaptan at an early period of the radiation-induced reaction, as shown in Table II. When the reaction is completed, the product is found to be mainly di-*n*-propylsulfide; also, the radiolysis of propylene with a smaller amount of hydrogen sulfide preferentially leads to the formation of di-*n*-propylsulfide rather than to that of *n*-propylmercaptan. Therefore, this reaction can be used for the preparation of

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[8] S. Iizuka, M. Hatada and K. Hirota, This Bulletin, 36, 817 (1963).

n-propylmercaptan or of di-*n*-propylsulfide if one properly adjusts the reaction conditions.

The Reaction Mechanism. — Both *n*-propylmercaptan and di-*n*-propylsulfide were found to be produced in the irradiation of the sample. *n*-Propylmercaptan is undoubtedly the free-radical addition product of hydrogen sulfide to propylene, while di-*n*-propylsulfide is the secondary addition product of *n*-propylmercaptan to propylene.

$$CH_2{=}CH{-}CH_3 + H_2S \rightarrow HSCH_2{-}CH_2{-}CH_3 \tag{1}$$

$$CH_2{=}CH{-}CH_3 + HSCH_2{-}CH_2{-}CH_3 \rightarrow (CH_3{-}CH_2{-}CH_2)_2S \tag{2}$$

Both yields increased with an increase in the irradiation time, as is shown in Fig. 1. Besides, a small amount of hydrogen was found, probably produced by the following termination reaction.

$$H\cdot + H_2S \rightarrow H_2 + HS\cdot \tag{3}$$

The hydrogen atom in Eq. 3 might be produced by the radiolysis of hydrogen sulfide:⁹⁾

$$H_2S \rightsquigarrow H\cdot + HS\cdot \tag{4}$$

A small amount of air was found to reduce the production of *n*-propylmercaptan and di-*n*-propylsulfide. Air apparently acts as a free radical scavenger to retard this chain reaction.

As has been discussed above, the reaction in all the cases is undoubtedly a free-radical chain reaction. The *G*-values calculated for the gamma ray-initiated experiments indicate that, in most cases, the kinetic chain is quite long.

Hydrogen sulfide is known to decompose the H atom and the HS radical.⁹⁾ These radicals can initiate a chain reaction in the following manner. As well as the reaction started by the radiolytically-generated HS radical in process 4, the HS radicals generated in the processes 6 and 3 would also lead to the chain propagation,

$$H_2S \rightsquigarrow HS\cdot + H\cdot \tag{4}$$

$$H\cdot + H_2C{=}CH{-}CH_3 \rightarrow H_3C{-}\dot{C}H{-}CH_3 \tag{5}$$

$$H_3C{-}\dot{C}H_3 + H_2S \rightarrow H_3C{-}CH_3{-}CH_3 + HS\cdot \tag{6}$$

$$H\cdot + H_2S \rightarrow H_2 + HS\cdot \tag{3}$$

$$HS\cdot + H_2C{=}CH{-}CH_3 \rightarrow HSCH_2{-}\dot{C}H{-}CH_3 \tag{7}$$

$$HSCH_2{-}\dot{C}H{-}CH_3 + H_2S \rightarrow HSCH_2{-}CH_2{-}CH_3 + HS\cdot \tag{8}$$

The reaction proceeds according to the chain mechanism shown by Eqs. 7 and 8, regenerating the sulfhydryl radical during these chain-propagating steps. Such a free radical chain mechanism is in good accord with the inhibiting effect of air. The great length of the chains precludes the ready detection of the saturated hydrocarbon or hydrogen formed in 6 and 3. Steps 7 and 8 are the chain-carrying steps, their length depending upon the processes of radical termination, which may occur either at walls or by recombination in the system.

n-Propylmercaptan, once formed, undergoes further reaction with propylene to give di-*n*-propylsulfide. The free radical addition of thiols to olefins, which has been studied extensively,¹⁰⁾ is considered to involve the following chain-propagating steps:

$$C_3H_7SH \rightsquigarrow H\cdot + C_3H_7S\cdot \tag{9}$$

$$C_3H_7S\cdot + CH_2{=}CH{-}CH_3 \rightarrow C_3H_7SCH_2{-}\dot{C}H{-}CH_3 \tag{10}$$

$$C_3H_7SCH_2{-}\dot{C}H{-}CH_3 + C_3H_7SH \rightarrow C_3H_7SCH_2{-}CH_2{-}CH_3 + C_3H_7S\cdot \tag{11}$$

Summary

The radiation-induced free radical addition of hydrogen sulfide to propylene to give *n*-propylmercaptan and di-*n*-propylsulfide has been studied. The direction of the addition to propylene is consistent with that of the radical addition to such olefins previously studied, suggesting that the SH is both the adding and chain-carrying species. The addition of the thiol to propylene has been found to undergo a free radical chain reaction, readily yielding di-*n*-propylsulfide in the succeeding step.

Department of Chemistry
Radiation Center of Osaka Prefecture
Sakai, Osaka (K. S. & W. A.)

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Kita-ku, Osaka (S. O.)

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9) E. C. Truesdale and S. C. Lind, *J. Am. Chem. Soc.*, **54**, 516 (1932).

10) A. Fontijn and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1384, 1397, 1410 (1957); K. Araki, T. Hoshino, S. Shida and K. Yamagishi, *Proceedings of the Second Symposium on Atomic Energy of Japan*, **4**, 158 (1958).