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THE PHOTO-ADDITION OF HYDROGEN SULFIDE TO OLEFINIC BONDS[1]

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Received July 1, 1942

The photo-addition of hydrogen sulfide to olefinic bonds is so easily and quickly effected that it should find numerous applications in organic syntheses. Radiation of wave length sufficiently short to dissociate hydrogen sulfide (*ca.* 2800 Å.U.) seems to be the primary requisite for initiation of reaction. A quartz mercury arc as a radiation source and a quartz reaction vessel readily fulfill this requirement. However, Pyrex may be substituted for quartz if a small amount of a photo-sensitizer, such as acetone, which can be dissociated by longer wave length radiation, is added to the reaction mixture. In accordance with the rule proposed by Posner (10) concerning the addition of mercaptans to double bonds, the sulfhydryl group acts as does the mercapto group and adds to the carbon atom bonded to the greater number of hydrogen atoms. In the case of terminal olefinic bonds the only products are the primary mercaptan and the di-normal sulfide which is formed by combination of the mercaptan and the olefin. Although the rate of addition varies greatly from compound to compound, the reaction usually approaches completion at room temperatures in a relatively short time.

Although we have been unable to find references to a similar clean cut addition of hydrogen sulfide, certain work with mercaptans may be pertinent. Posner (10) observed the addition of certain mercaptans to the double bond of unsaturated ketones and proved that the reaction could be extended to olefins. In 1934, Burkhardt (2) suggested that the addition of thiophenol to styrene might proceed as a chain reaction. Jones and Reid (4) showed that peroxides are catalysts for such additions. Kharasch, Read, and Mayo (6) have shown that the additions of thioglycolic acid to styrene and isobutene take place in accordance with Posner's rule and suggest that this reaction and previously observed mercaptan additions are catalyzed by the presence of oxygen or peroxide, which generate chain-initiating RS radicals. They term such addition "abnormal," that is, contrary to an admittedly arbitrary extension of Markownikoff's Rule. Kaneko (5), in synthesizing $CH_3SCH_2CH_2CH_2OH$ by addition of methylmercaptan to allyl alcohol, indicates that daylight, in conjunction with mercury methylmercaptide and oxygen, greatly accelerates reaction, but that it is ineffective in the absence of the latter two materials.

The literature indicates that addition of hydrogen sulfide to double bonds takes place only under rather severe conditions. A number of workers have studied the reaction and have employed temperatures from 200° to 750°, various catalysts, and usually superatmospheric pressure. In general, the yields are relatively low and a complex mixture of isomers and by-products results. The

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at its 103rd meeting, Memphis, Tennessee, April 20–23, 1942.

review by Mayo and Walling (8) is a concise summary of the field of hydrogen sulfide-olefin reactions.

MATERIALS AND TECHNIQUE

Hydrogen sulfide (Ohio Chemical) was collected in a liquid air-cooled trap, thoroughly degassed and distilled under vacuum from a trap cooled by solid carbon dioxide to one in liquid air. The 1-butene, propylene, diallyl, and vinyl chloride were the materials previously purified (12). Laboratory samples of diallyl ether and methyl acrylate were refractionated.

The techniques of both liquid- and gas-phase experiments were those described in the paper on the photo-addition of hydrogen bromide (12). Briefly, the reactants were distilled under a high vacuum into a bomb tube reactor (usually of quartz) which was sealed off and then exposed to radiation from a quartz mercury arc lamp. Selected temperatures were maintained by immersing the reactor in a transparent liquid bath contained in a larger quartz vessel.

DISCUSSION

Hydrogen sulfide shows continuous absorption beginning at *ca.* 2800 Å.U. and is photochemically decomposed with a quantum efficiency of the order of unity into hydrogen and sulfur. In the decomposition H atoms and HS radicals are formed (11). These particles can initiate a chain reaction in the following manners:

$$\text{(a)} \qquad H_2S \xrightarrow{h\nu} H + HS$$

$$\text{(b)} \qquad H + H_2C{=}CHR \longrightarrow H_3C\overset{|}{C}HR$$

$$\text{(c)} \qquad H_3C\overset{|}{C}HR + H_2S \longrightarrow H_3CCH_2R + HS$$

$$\text{or (d)} \qquad H + H_2S \longrightarrow H_2 + HS$$

Both (c) and (d) would also lead to the chain begun by the photo-generated HS radical:

$$\text{(e)} \qquad HS + H_2C{=}CHR \longrightarrow HSCH_2\overset{|}{C}HR$$

$$\text{(f)} \qquad HSCH_2\overset{|}{C}HR + H_2S \longrightarrow HSCH_2CH_2R + HS$$

The length of the chains precludes the ready detection of the saturated hydrocarbon or hydrogen formed in (c) and (d). Steps (e) and (f) are the chain-carrying steps and their length would be dependent upon processes of radical destruction which might occur in the system, as at walls or by recombination. The energetics of the various reactions, as roughly based upon bonding energies (9), are almost exactly the same as those involved in the analogous case of the photo-addition of hydrogen bromide to olefins.

With longer wave length radiation, the "abnormal" reaction can be sensitized by materials which are decomposed into radicals by such quanta. Thus, for example, acetone is dissociated at *ca.* 3200 Å.U. into CH_3 and $CH_3\overset{|}{C}{=}O$; either of these particles can remove an H atom from H_2S, giving an HS radical which can enter into the reaction (e).

EXPERIMENTAL

LIQUID-PHASE REACTION—SIMPLE OLEFINS

1-Butene (0.044 mole) and hydrogen sulfide (0.088 mole) sealed in a 10 mm. I.D. quartz tube were illuminated for four minutes at 0°C with the full radiation of a quartz mercury arc. After chilling in solid carbon dioxide the tube was opened, and the unreacted material evaporated off. The product (3.8 cc.) was shaken with a large excess of 10% sodium hydroxide solution and the supernatant liquid removed. This amounted to 0.5 cc. and had a refractive index n_D^{20} 1.4530. A sample of Eastman di-*n*-butyl sulfide (redistilled) gave n_D^{20} 1.4533; literature value (1), 1.4529. The alkaline solution was acidified with hydrochloric acid and the regenerated product analyzed by refractive index and boiling point: Found: n_D^{20} 1.4431; b.p. 98.0°. Redistilled Eastman *n*-butylmercaptan had a boiling range 98.0–98.2° and gave refractive indices *n*. 1.4426 and n_D^{25} 1.4400. Ellis and Reid (3) give n_D^{25} 1.4401 for *n*-butylmercaptan and 1.4338 for the secondary isomer. Approximately 80% of the 1-butene reacted during these four minutes and the product is apparently practically pure *n*-butylmercaptan (*ca.* 85%) and di-*n*-butyl sulfide (15%).

The same experiment was repeated at −78°. In this case, 40–45% of the butene reacted in four minutes. The product which contained *ca.* 5% sulfide was treated with sodium plumbite solution and the precipitate washed first with water, then with acetone, and dried. The mercaptan was regenerated with dilute hydrochloric acid and dried; its refractive index was n_D^{20} 1.4431.

Propylene and hydrogen sulfide in a sealed quartz tube combine quickly and smoothly when illuminated with the Uviarc lamp. More than 95% of the propylene was consumed when an equal volume mixture of the liquid reactants (6.5 cc. each) was irradiated for six minutes at 0°. The product was 65 wt.-% *n*-propylmercaptan and 35% di-*n*-propyl sulfide. The mercaptan boiled at 67.5° and had indices of n_D^{20} 1.4380 and n_D^{25} 1.4351. Ellis and Reid (3) give for the same constants 67.4–67.6° and n_D^{25} 1.4351, respectively. The sulfide had an index n_D^{20} 1.4480 and the boiling point 141.5°. The boiling point given in the literature is 141.5–142.5 (7) and the refractive index at 20°, 1.4481 (1).

The effectiveness of acetone in sensitizing the chain reaction is demonstrated by the following experiment: Two sealed Pyrex tubes, one containing 3.7 cc. each of propylene and hydrogen sulfide, and the other the same mixture plus an added 0.5 cc. of acetone, were illuminated at 0° for six minutes. In the first case, only 0.2 cc. of product was obtained, while in the second case, 75% of the propylene had reacted, giving 3.5 cc. of product, which was 80 wt.-% *n*-propylmercaptan and 20% di-*n*-propyl sulfide.

LIQUID PHASE—OTHER UNSATURATES

The photo-addition of hydrogen sulfide to the double bond offers a new method for preparing other interesting sulfur derivatives, *e.g.*, ethylene thiochlorohydrin is readily prepared from vinyl chloride.

$$H_2S + H_2C{=}CHCl \xrightarrow{h\nu} HSCH_2CH_2Cl$$

A secondary product is also readily formed which is extremely vesicant and is presumably β,β'-dichlorodiethyl sulfide.

$$ClCH_2CH_2SH + ClCH{=}CH_2 \xrightarrow{h\nu} (ClCH_2CH_2)_2S$$

Hydrogen sulfide (9 cc.) and vinyl chloride (10 cc.) in a quartz reactor were frozen in liquid air and the evacuated tube sealed off. The contents were illuminated by the quartz mercury arc for ten minutes at room temperature. Immediately on illumination, the tube contents boiled quietly; this ceased if the light was cut off, but began again upon irradiation. After evaporating off the unreacted hydrogen sulfide and vinyl chloride, 10 cc. of vile smelling product remained. A micro-distillation of this material gave 4.5 cc. of product boiling at 93–108° which was analyzed for sulfur and chlorine:

Anal. Calc'd for C_2H_5ClS: Cl, 36.7; S, 33.2.
Found: Cl, 38.0; S, 31.3.

These results suggest that a small amount of vinyl chloride dimer may be present in the product. No sharply defined fractions boiling above this region were isolated. The yield based upon the amount of vinyl chloride reacting is 70–80%; somewhat more than half of this product is probably β,β'-dichlorodiethyl sulfide. Its characteristic delayed vesicant action was confirmed by exposing a small patch of skin on the forearm to the vapors for 15 minutes.

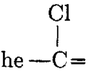
As in the case with 1-butene, photo-addition of hydrogen sulfide to vinyl chloride is slower at −78°. When an equal volume mixture of these compounds (9 cc. of each) was illuminated at the lower temperature for ten minutes, 4 cc. of product was left after distilling off the hydrogen sulfide and vinyl chloride. Chlorine and sulfur analyses of the product are as ollows:

Anal. Calc'd for $C_4H_6Cl_2S$: Cl, 45.2; S, 20.4.
Found: Cl, 39.6; S, 26.7.

Evidently, the product is a mixture of the sulfide and mercaptan (*cf.* theoretical chlorine-sulfur composition to the thiochlorohydrin).

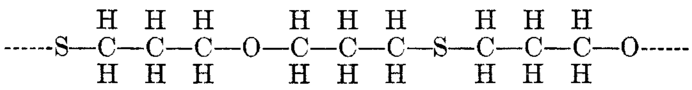
Hydrogen sulfide addition to the more highly substituted ethylenes, *e.g.*, 2-chlorobutene-2, is considerably slower. Four and five-tenths cubic centimeters of 2-chlorobutene-2 and 2.7 cc. of hydrogen sulfide were sealed off in the quartz reactor and illuminated with the quartz mercuy arc for ten minutes at −78°. After evaporating and distilling off the unreacted materials, about 0.5 cc. of crude product remained. The admittedly impure material was analyzed for sulfur and hydrolyzable chlorine; the latter value was determined by potentiometric titration both in sodium acetate and in acid solution.

Found: Sulfur–19.0, 19.8%; 0.59, 0.62 eq./100 g.
Hydrolyzable chlorine, in sodium acetate solution; 0.56 eq./100 g.
Hydrolyzable chlorine, in acid solution; 0.57 eq./100 g.

It seems improbable that chlorine would have been retained in the molecule if the —SH group had added to the  $\overset{\overset{\text{Cl}}{|}}{\text{—C=}}$ side of the double bond, and the near equality of the hydrolyzable chlorine and sulfur content speaks for the formation of the thiochlorohydrin.

Following the same technique, hydrogen sulfide is easily added to diallyl or diallyl ether to give high molecular weight compounds. Thus for diallyl ether:

$$(CH_2{=}CHCH_2)_2O + H_2S \xrightarrow{h\nu}$$



$$\cdots\cdots S-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-S-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O\cdots\cdots$$

By treating diallyl with hydrogen sulfide at 0°, a liquid was obtained which contained 30.9% total sulfur and 16.3% mercaptan sulfur; its average molecular weight was 210. Product from the reaction of diallyl ether with hydrogen sulfide had a molecular weight of 285 and contained 25.9% total sulfur.

Methyl acrylate and allyl alcohol reacted with hydrogen sulfide with difficulty at 0°; a small amount of product, which was precipitated with Pb^{++} and Ag^{+} ions, was obtained in each case. Because of the small quantities involved, no analyses were attempted.

GAS-PHASE REACTION

The gas-phase photo-addition of hydrogen sulfide to 1-butene is slow. When 99.2 mm. of 1-butene and 201.5 mm. of hydrogen sulfide in a one-liter Pyrex bulb were illuminated for two hours by the quartz mercury arc, there was no pressure change. Acetone (19.5 mm.)

was then added to sensitize reaction. After four hours, the pressure decreased 20 mm. The product was washed free of acetone and a refractive index taken.

Product n_D^{20}	1.4487
n-C_4H_9SH	1.4426
$(n$-$C_4H_9)_2S$	1.4533

Pressure decrease was somewhat more rapid when the reaction of the same proportions of gases was carried out in a quartz vessel. It amounted to 18 mm. in 25 minutes (initial pressure 304 mm.), and 111 mm. in three hours. Product formed in the small quartz vessel was insufficient for analysis, but a portion of it seemed to be sulfur dust from the photolysis of hydrogen sulfide. Hydrogen was also present.

SUMMARY

1. Short wave length ultra-violet radiation readily promotes the addition of hydrogen sulfide to olefins to form mercaptans and sulfides.

2. Light of wave length transmittible by Pyrex is effective in initiating reaction if a small amount of photo-dissociable material such as acetone is present.

3. The sulfur of the sulfhydryl or mercapto group adds exclusively to the carbon atom of the double bond having the larger number of hydrogen atoms.

4. Hydrogen sulfide and olefin combine slowly in the gas phase under the influence of ultra-violet radiation.

5. The mechanism is one of a free radical chain and is dependent upon the preliminary dissociation of hydrogen sulfide.

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