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REACTIONS OF HYDROGEN SULFIDE WITH VARIOUS ORGANIC COMPOUNDS AT HIGH PRESSURES[1]

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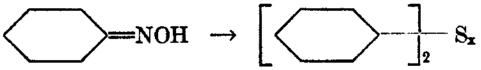
A recent paper from this laboratory (1) describes the reaction of aldehydes and ketones with hydrogen sulfide under pressure to give *gem*-dithiols and polysulfides.

$$R_2CO \xrightarrow{H_2S} H_2O + R_2C(SH)_2 + (R_2CH)_2S_x \qquad (x = 2\text{–}4)$$

The present paper describes research extending the knowledge of the effect of high pressures on the reactivity of hydrogen sulfide with other classes of compounds. At a pressure of 8500 atmospheres with temperatures of 125–150°, hydrogen sulfide is a powerful reducing agent capable of converting methyl formate, ethyl formate, acetamide, thioacetamide, and cyclohexanone oxime to polysulfides.

$$HCO_2R \rightarrow ROH + (CH_3)_2S_x \qquad (x = 2\text{-}5)$$

$$CH_3CONH_2 \text{ or } CH_3CSNH_2 \rightarrow (CH_3CH_2)_2S_3$$



Ethyl acetate, triethyl orthoformate, and diethyl acetal are similarly converted to polysulfides if triethylamine is present.

$$CH_3CO_2C_2H_5 \text{ or } CH_3CH(OC_2H_5)_2 \rightarrow (C_2H_5)_2S_x \qquad (x = 2, 3)$$
$$HC(OC_2H_5)_3 \rightarrow (CH_3)_2S_x + C_2H_5OH$$

The importance of high pressure in bringing about these conversions was shown by the fact that no appreciable amounts of polysulfides were formed when several of the experiments were repeated at autogenous pressure.[2]

Besides the above reactions, which are apparently new, several well-known reactions of hydrogen sulfide are facilitated by high pressure. Thus, acetonitrile gave thioacetamide at 80° under a pressure of 8500 atmospheres, but not under autogenous pressure. Benzonitrile and α-hydroxyisobutyronitrile also gave thioamides at 8500 atmospheres. The formation of thioamides from nitriles and hydrogen sulfide at ordinary pressures generally requires a base (10) or a combination of a silica-alumina catalyst and a high temperature (4). *tert*-Butyl alcohol and *n*-butyl alcohol gave the corresponding mercaptans at 180° and a pressure of 8500 atmospheres; no appreciable amount of mercaptan was formed from

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[2] "Autogenous pressure" in this paper means the internal pressure in an autoclave that has been filled not more than half full with approximately equal volumes of a reactant and liquid hydrogen sulfide, sealed, and then heated to 80–300°. It is commonly 50–100 atm. and seldom exceeds 200 atm.

tert-butyl alcohol at autogenous pressure. Apparently the conversion of alcohols to mercaptans occurs at ordinary pressures only if higher temperatures and a catalyst are used (9). Tetraisobutylene was converted to a mercaptan at 8500 atmospheres under conditions that gave only a trace of mercaptan at autogenous pressure, showing that the addition of hydrogen sulfide to olefins is also aided by high pressure.

High pressure can enhance the reactivity of mercaptans as well, for at 8500 atmospheres, but not at 1000 atmospheres or lower, ethyl mercaptan reacted with ethyl formate to give triethyl trithioorthoformate.

$$HCO_2C_2H_5 + 3\ C_2H_5SH \rightarrow HC(SC_2H_5)_3 + C_2H_5OH + H_2O$$

EXPERIMENTAL

Experiments with hydrogen sulfide under a pressure of 8500 atmospheres. Table I shows the conditions and results of these experiments. The experiment with methyl formate is described below in detail to illustrate the operation of the pressure equipment and some of the methods used to isolate and identify the products.

Methyl formate (3.79 g.), hydrogen sulfide (3.00 g.), and nitrogen (0.15 g.) were put in a stainless-steel cylinder with a movable piston. The nitrogen was used to ensure return of the piston at the end of the experiment when the external pressure on it was released. The cylinder was placed in a Bridgman-type pressure apparatus (2) and its contents were subjected to a pressure of 8500 atm. at 125°. After 15 hours, during which time the initial pressure had fallen to 7300 atm., the apparatus was cooled, the pressure was released, and the cylinder was taken out and vented. The loss of weight on venting indicated that 2.59 g. hydrogen sulfide had reacted. The product was taken from the cylinder and combined with the products of seven similar runs. A total of 30.4 g. of methyl formate and 19.7 g. of hydrogen sulfide was used in the eight runs. The product consisted of 20.0 g. of an aqueous solution and 26.1 g. of a heavy yellow oil. Distillation of the aqueous solution gave 4.5 g. of methyl formate, 5.10 g. of water, and 5.94 g. of methanol (n_D^{19} 1.3388; b.p. 60–63.5°; m.p. and mixture m.p. of 3,5-dinitrobenzoate, 106–107°).

Heating the yellow oil at 60°/1 mm. separated it into A, 3.2 g. of volatile oil; and B, 21.9 g. of nonvolatile oil. By distilling Fraction A through a 13 cm. x 0.6 cm. vacuum-jacketed glass tube containing a glass spiral, 0.53 g. of methyl disulfide (3, 5), b.p. 50–66°/97 mm., n_D^{25} 1.5272; and 0.91 g. of methyl trisulfide (5), b.p. 54–55°/11 mm., n_D^{25} 1.5878, were isolated. The infrared absorption spectra of the disulfide and trisulfide were identical with those of authentic samples.

Fraction B, d_4^{25} 1.5099, was soluble in cold benzene, chloroform, pyridine, or carbon disulfide, insoluble in most other solvents. Sulfur was formed when it was treated with cold 12 *N* nitric acid or hot 96% sulfuric acid. Its infrared absorption spectrum, like the spectra of methyl disulfide and methyl trisulfide, had a band at 7.05 μ probably caused by methyl groups. Reduction with lithium aluminum hydride by a previously described procedure (1) gave methyl mercaptan (6% yield) and hydrogen sulfide (15% yield), which were isolated as methyl 2,4-dinitrophenyl sulfide (m.p. and mixture m.p. 122–124°) and bis-(2,4-dinitrophenyl) sulfide (m.p. and mixture m.p. 189–191°). Like methyl pentasulfide (6), fraction B gave a red color with piperidine and decomposed on attempted distillation at 1 mm. These facts, together with the analytical data for fraction B, indicate that it is methyl pentasulfide mixed with small quantities of other methyl polysulfides, particularly the tetrasulfide. Methyl tetrasulfide is a distillable compound (7) and therefore cannot be present in large amount.

Anal. Calc'd for $C_2H_6S_5$: C, 12.7; H, 2.7; S, 84.7.

Found: C, 13.4; H, 2.85; S, 81.8.

Experiments with hydrogen sulfide at autogenous pressure.[2] A 1-l. stainless-steel autoclave

TABLE I

PRODUCTS OBTAINED BY HEATING VARIOUS ORGANIC COMPOUNDS WITH HYDROGEN SULFIDE UNDER AN INITIAL PRESSURE OF 8500 ATMOSPHERES

REACTANTS	H_2S REACTED, G.	TEMP., °C.[c]	PRODUCTS ISOLATED (WITH YIELD[a])
Methyl formate (30.4 g.), H_2S (19.7 g.)[b]	19.7	125	Methyl formate[e] (4.5 g., 15% recovery), methanol[e] (5.95 g., 63%), water[e] (5.10 g., 66%), methyl disulfide[e, f] (0.53 g., 2.3%), methyl trisulfide[e, g] (0.91 g., 2.8%), crude methyl pentasulfide (21.9 g., 45%)
Ethyl formate (21.9 g.), H_2S (18.6 g.)[b]	18.3	125	Ethanol[e, f] (9.87 g., 69%), water[e] (4.36 g., 82%) methyl disulfide[e, f] (0.60 g. 4%), methyl trisulfide[e, f] (0.67 g., 4%), crude methyl pentasulfide (19.6 g., 70%)
Methyl acetate (1.8 g.) H_2S (1.2 g.)		150	Little reaction occurred
Ethyl acetate (11.9 g.), triethylamine (1.11 g.), H_2S (9.3 g.)[b]	6.3	150	Ethyl disulfide[e, f] (1.91 g., 6%), ethyl trisulfide[e, g] (3.58 g., 9%), acetic acid[e, k] (0.94 g., 12%)
Acetamide (12.1 g.), H_2S (9.4 g.)[b]	7.3	125	Acetamide[i] (7.4 g., 61% recovery), ethyl trisulfide[e, f] (1.62 g., 10%), sulfur[i] (1.70 g., 19%), amnonia
Thioacetamide (4.0 g.), methanol (4.0 g.), H_2S (5.5 g.)[b]	3.7	125	Ethyl trisulfide[e] (2.0 g., 49%)
Acetonitrile (2.99 g.), H_2S (3.26 g.)	3.0	80[n]	Thioacetamide[g, i] (4.5 g., 83%)
Benzonitrile (3.94 g.), H_2S (2.31 g.)	2.2	100	Thiobenzamide[g, i] (1.66 g., 32%), benzonitrile[e] (0.51 g., 13% recovery)
α-Hydroxyisobutyronitrile (3.67 g.), H_2S (2.63 g.)	1.2	30	α-Hydroxythioisobutyramide[l] (2.99 g., 58%)
Triethyl orthoformate (10.5 g.), triethylamine (1.11 g.), H_2S (7.9 g.)[b]	6.1	125	Ethanol[e, f] (9.2 g., 94%), methyl polysulfides (3.1 g.), sulfur[i] (0.77 g.)
Diethyl acetal (9.8 g.), triethylamine (1.1 g.), H_2S (7.2 g.)[b]	4.7	150	Ethyl disulfide[e, f] (1.94 g., 38%), ethyl trisulfide[e] (1.96 g., 31%)
Cyclohexanone oxime (2.50 g.), methanol (1.92 g.), H_2S (2.47 g.)	2.0	60	Cyclohexyl polysulfides[d] (2.24 g., 69%)
tert-Butyl alcohol (1.52 g.), H_2S (1.64 g.)		180	*tert*-Butyl mercaptan[e, h] (0.63 g., 34%)

TABLE I—*Continued*

REACTANTS	H_2S REACTED, G.	TEMP., °C[c]	PRODUCTS ISOLATED (WITH YIELD[a])
n-Butyl alcohol (6.43 g.), H_2S (5.17 g.)[b]	1.3	180	*n*-Butyl alcohol[e] (1.77 g., 27% recovery), 1-butanethiol[h] (0.40 g., 5%), *n*-butyl ether[e, f] (0.55 g., 10%), *n*-butyl sulfide[e, f] (2.09 g., 33%)
Methanol (2.37 g.), H_2S (2.42 g.)	0.0	125	Methyl mercaptan[h] (0.01 g., 0.3%)
Tetraisobutylene[o] (15.8 g.), α,α'-azodiisobutyronitrile (0.20 g.), H_2S (13.0 g.)[b]	?	80	Tetraisobutylene (10.6 g., 67% recovery), $C_{16}H_{33}SH$[m] (2.69 g., 15%)

[a] No allowance has been made for recovered starting material in calculating per cent yields. [b] The products of several runs were combined and worked up together. [c] Reaction time was 14–15 hours. [d] The polysulfide mixture, b.p. 116–169°/1.2 mm., n_D^{25} 1.6124, gave cyclohexanethiol on reduction with $LiAlH_4$. *Anal.* Calc'd for $C_{12}H_{22}S_4$: C, 48.9; H, 7.5; S, 43.6. Found: C, 49.5; H, 7.3; S, 44.5. [e] B.p. and n_D^{25} agreed with reported values. [f] Infrared absorption spectrum identical with that of authentic sample. [g] Had expected elemental composition. [h] The corresponding alkyl 2,4-dinitrophenyl sulfide was identified by the method of mixed melting points. *tert*-Butyl 2,4-dinitrophenyl sulfide, m.p. 109–110°, is new. *Anal.* Calc'd for $C_{10}H_{12}N_2O_4S$: C, 46.9; H, 4.7; S, 12.5. Found: C, 47.1; H, 4.8; S, 12.8. [i] Identified by the method of mixed melting points. [j] M.p. 115–116°, as reported (11). [k] Gave positive iodine-lanthanum nitrate test (12). [l] A new compound, easily soluble in water or ethanol; m.p. 80–81° after crystallization from benzene. *Anal.* Calc'd for C_4H_9NOS: C, 40.3; H, 7.6; S, 26.9. Found: C, 40.7; H, 8.0; S, 27.1. [m] B.p. 76–83°/0.5 mm., n_D^{25} 1.4748; it is probably a mixture of isomeric mercaptans. *Anal.* Calc'd for $C_{16}H_{34}S$: C, 74.4; H, 13.3; S, 12.4; SH, 12.8. Found: C, 74.9; H, 13.2; S, 11.7; SH, 14.9 (confirmed by infrared absorption spectrum). [n] At higher temperatures much $(C_2H_5)_2S_x$ is formed. [o] A mixture of isomers (13).

containing 147 g. of methyl formate was cooled to −80° and evacuated to a pressure of 20 mm. Hydrogen sulfide (150 g.) was distilled into the autoclave, which was then rocked at 295° for 14 hours. Most of the methyl formate was recovered unchanged by distillation of the reaction mixture. The material not volatile from a still-pot at 100°/760 mm. was a yellow oil weighing only 2.8 g. Its refractive index, n_D^{25} 1.3536, shows that it did not contain much methyl polysulfide.

Under similar conditions there was obtained no appreciable amount of methyl polysulfides from methyl formate at 150° or 225°; of methyl polysulfides from methyl formate in the presence of 10% of triethylamine at 200°; of ethyl polysulfides from ethyl acetate in the presence of 10% of triethylamine at 150° or 225°; of thioacetamide from acetonitrile at 80°; or of *tert*-butyl mercaptan from *tert*-butyl alcohol at 180°. The yield of $C_{16}H_{33}SH$ from tetraisobutylene in the presence of α,α'-azodiisobutyronitrile at 85° and autogenous pressure was less than 1% (experiment by Dr. P. J. Graham).

Triethyl trithioorthoformate from ethyl formate. A mixture of 2.74 g. of ethyl formate and 4.16 g. of ethyl mercaptan was heated at 150° for 17 hours under a pressure of 8500–7600 atm. Distillation of the reaction mixture gave 1.79 g. (41% yield) of crude triethyl trithioorthoformate, b.p. 60–65°/0.6 mm. Redistillation gave a fraction whose infrared absorption spectrum and other physical constants (b.p. 83°/1.5 mm., n_D^{25} 1.5362) were identical with those of authentic triethyl trithioorthoformate (8).

When the experiment was repeated at 1000 atm. or at autogenous pressure, no appreciable amount of triethyl trithioorthoformate was formed. The yield was only 10–15% when the experiment was repeated at 125° and 8500 atm.

SUMMARY

Hydrogen sulfide has greatly increased reactivity at a pressure of 8500 atmospheres. At this pressure it can convert such compounds as methyl formate, ethyl acetate, acetamide, and cyclohexanone oxime to alkyl polysulfides. Moreover, several previously known reactions of hydrogen sulfide are facilitated by such a pressure.

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REFERENCES

(1) CAIRNS, EVANS, LARCHAR, AND McKUSICK, *J. Am. Chem. Soc.*, **74**, 3982 (1952).
(2) BRIDGMAN, *The Physics of High Pressure*, Bell and Sons, London, 1949, pp. 30–59.
(3) McALLAN, CULLUM, DEAN, AND FIDLER, *J. Am. Chem. Soc.*, **73**, 3627 (1951).
(4) MAHAN (to Phillips Petroleum Co.), U. S. Patent 2,421,031 (1947).
(5) KUSHNER, GORIN, AND SMYTH, *J. Am. Chem. Soc.*, **72**, 477 (1950).
(6) RIDING AND THOMAS, *J. Chem. Soc.*, **123**, 3271 (1923).
(7) FUSON, PRICE, BURNESS, FOSTER, HATCHARD, AND LIPSCOMB, *J. Org. Chem.*, **11**, 487 (1946).
(8) HOLMBERG, *Ber.*, **40**, 1740 (1907).
(9) KRAMER AND REID, *J. Am. Chem. Soc.*, **43**, 880 (1921); BAUER (to I. G. Farbenindustrie), U. S. Patent 2,116,182 (1938); LAUGHLIN (to Standard Oil Development Co.), U. S. Patent 2,514,300 (1950).
(10) TROEGER AND EWERS, *J. prakt. Chem.*, [2] **60**, 520 (1899); KINDLER, *Ann.*, **431**, 187 (1923); OLIN AND JOHNSON, *Rec. trav. chim.*, **50**, 72 (1931); RALSTON, VANDER WAL, AND McCORKLE, *J. Org. Chem.*, **4**, 68 (1939).
(11) KINDLER, *Ann.*, **431**, 201 (1923).
(12) FEIGL, *Qualitative Analysis by Spot Tests*, Elsevier Co., New York, 1946, p. 397.
(13) COSBY, *The Structures of the Tetraisobutylenes*, Univ. Microfilms (Ann Arbor, Mich.) Pub. No. 352 (1941); JOHNSON, *The Oxidation of Tetraisobutylene*, Univ. Microfilms (Ann Arbor, Mich.), Pub. No. 342 (1941).