

The Production of Hydrogen Selenide by Heating Paraffine with Selenium in the Presence of a Catalyst

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The production of hydrogen sulfide by heating hydrocarbons with sulfur has been widely studied and industrially applied. The production of hydrogen selenide by a similar process has been investigated by A. Etard and H. Moissan¹ employing colophene at a reaction temperature of 300°C. G. M. Weber² reported a poor yield by this method and stated that only 30.8% of the gas produced was hydrogen selenide. Green and Bradt³ have reported that 1.0 g. of selenium heated at 380°C. with 50 g. paraffine-base motor oil for 1.0 hour produced 96.8% of the theoretical yield of hydrogen selenide and also that the yield of selenide from the mixture was negligible at temperatures below 300°C.

Scudder and Lyons⁴ found that the production of hydrogen sulfide by heating hydrocarbons and sulfur could be catalyzed by finely divided carbon. The present work is a study of the effect of carbon in the mixture of paraffine and selenium for the production of hydrogen selenide.

Experimental

An intimate mixture of hydrocarbon, selenium, catalyst, etc., was placed in a 12x1 inch Pyrex test tube, equipped with a rubber stopper, through which were inserted a thermometer, a piece of tubing with fused-in stopcock, and a gas delivery tube leading to the absorption chamber, which contained a 5% solution of cupric sulfate to react with the hydrogen selenide, yielding cupric selenide as a precipitate.

The Pyrex tube was suspended in an electrically heated chamber. The thermometer bulb was in direct contact with the reaction mixture. At the end of the heating period, dry hydrogen was passed for 15 minutes through the glass-stopcocked tube into the reaction chamber to carry all hydrogen selenide into the copper solution. The cupric selenide was quantitatively collected on a weighed filter paper, washed, dried, and weighed.

A mixture of 10 g. white paraffine, M.P. 60°C., and 0.25 g. of powdered metallic selenium was heated to 360°-370°C. for 1 hour after the temperature of the reactants reached 360°C. and the hydrogen selenide calculated from the weight of cupric selenide recovered. The average of two experiments was 21.2% of theory.⁵

Accepting this as the normal yield obtainable under the described conditions, we planned a series of experiments to determine the effect of the presence of certain addition agents on the formation of selenide under the following conditions: Temperature, 360°-370°C.; time limit, 1 hour only after reactants reached 360°.

The data collected from a series of twelve experiments are given in Table I.

¹J. W. Mellor, 1930. Treatise on inorganic and theoretical chemistry 10:760.

²C. Green and W. E. Bradt, 1934. Proc. Indiana Acad. Sci. 43:116.

³E. D. Scudder and R. E. Lyons, 1931. Proc. Indiana Acad. Sci. 40:185.

⁵Green and Bradt reported a yield of 74.6% hydrogen selenide from heating 50 g. paraffine and 1g. selenium for 1 hour at 360°C.

TABLE I.

Exp.	Paraffine ¹ g.	Selenium ² g.	Pumice ³ g.	Addition Agent g.	H ² Se Yield %
1	10	0.25	0	0	21.2
2	10	0.25	0	Norite 3	45.0
3	10	0.25	5p	0	17.1
4	10	0.25	5p	Norite 3	63.7
5	5	0.125	5p	Norite 1.5	60.4
6	5	0.125	5c	Norite 1.5	75.0
7	5	0.125	5p	Bone Black 1.5	43.0
8	5	0.125	5c	Bone Black 1.5	45.9
9	5	0.125	5p	Charcoal ⁴ 1.5	57.4
10	5	0.125	5p	Lamp Black ⁵ 1.5	16.4
11	5	0.125	5c	Lamp Black 1.5	28.6
12	10	0.25	0	Norite 3	62.7

¹White paraffine wax, M.P. 60°C.²Finely powdered metallic selenium.³Pumice: p (powdered); c (coarse—about ¼ inch dia.).⁴Granular Coconut charcoal—about ¼ inch dia.⁵Wilkes, Martin Wilkes' "Ordinary Black".⁶A repetition of Exp. 2, except the charge was heated for 2 hours after the temperature of the reactants reached 360°C.

Summary

It has been found that finely divided carbon catalyzes the reaction between paraffine and selenium for the production of hydrogen selenide. Of the four carbon preparations studied, Norite was found the most effective. Pumice served as a catalytic support only; it alone was found to have no positive catalytic effect.