153. *The Photochemistry of Selenium. Part I. The Photochemical Oxidation of Hydrogen Selenide.*

By D. J. G. Ives and R. W. Pittman.

It is shown that for the oxidation of hydrogen selenide by gaseous oxygen the presence of liquid water is necessary. Also, that this reaction is promoted by light in the visible and the near ultraviolet and is autocatalysed by the production of solid selenium.

This paper introduces a systematic study of the hitherto-unrecorded photo-oxidation of hydrogen selenide and is mainly concerned with qualitative observations. These form the basis of future studies of the kinetics and mechanism of this and allied reactions.

In this investigation, known mixtures of hydrogen selenide and oxygen were exposed to a constant light flux from a mercury arc, the rate of oxidation being followed by the pressure change which accompanies the reaction $H_2Se + \frac{1}{2}O_2 = H_2O + Se$. The initial water content of the system was controlled, in amount, by the introduction of weighed quantities of water and, in location, by slight local cooling of the reaction vessel, which was otherwise maintained at a constant temperature of 25°. The method is described in detail in the experimental section.

It has been found that the oxidation of hydrogen selenide occurs rapidly only in the presence of liquid water in contact with illuminated selenium to which oxygen gas has access. The various points in this statement have been established in a number of experiments which are described in the appropriate order.

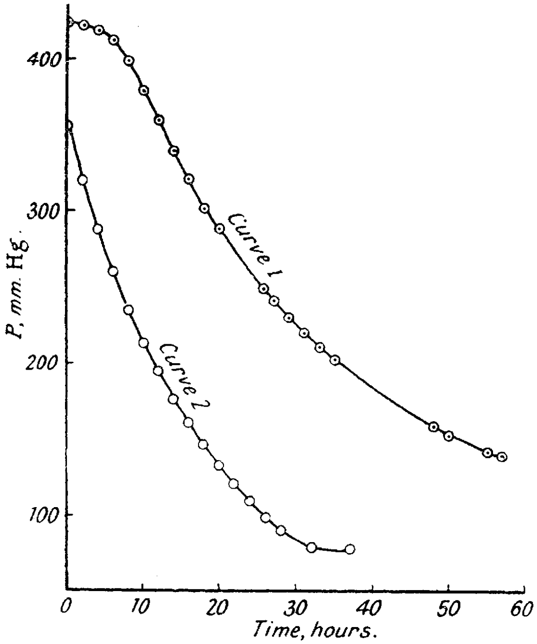
In the first of these, a dry mixture of the two gases in roughly stoicheiometric proportion at a total pressure of 160 mm. in a clean reaction bulb was illuminated for 70 hours. The fall of pressure was 0·6 mm. and the thin, transparent deposit of red selenium which was formed on the interior, illuminated surfaces of the vessel was found, on recovery, to weigh 3·7 mg. The formation of this weight of selenium by oxidation requires a pressure decrement of 3·0 mm. The deposition of selenium therefore appeared to be due to photolysis of the hydride by light in the near ultraviolet (Goodeve and Stein, *Trans. Faraday Soc.*, 1931, **27**, 393; Moser and Doctor, *Z. anorg. Chem.*, 1921, **118**, 284). A similar dry mixture and a mixture of 50% humidity (12 mm. water-vapour pressure at 25°), both set up in vessels containing a film of selenium deposited in previous experiments, showed no decrease of pressure on illumination for long periods. It is therefore apparent that, under the conditions of experiment, hydrogen selenide has little tendency to oxidise in the absence of liquid water, whether selenium is present or not.

A mixture containing sufficient water to exceed the limit of saturation and ensure the presence of a liquid film on the upper part of the vessel, where the light entered, showed markedly different behaviour. A very slow decrease of pressure occurred over a period of some hours in dull light; on illumination, however, the rate of fall of pressure increased. After some hours, when steady reaction conditions had been established, the light was interrupted several times. During the resulting dark periods the rate fell very nearly to zero, indicating that the reaction is mainly photochemical in nature.

The pressure changes which occurred in a similar experiment during which illumination was continuous are shown in Fig. 1, Curve 1; it will be seen that over the first 10 hours the rate of reaction gradually increased to a maximum. This increase of rate was accompanied by the formation of a film of red selenium on the initially clean surface of the reaction vessel, mainly within the area of illumination. Subsequently, the selenium deposit suffered remarkable changes as the oxidation proceeded. At first, it was in the form of a fairly uniform, red, opaque film, but after a few hours, the selenium appeared to " dissolve " and then " recrystallise " as reddish-black, granular aggregates, which later coalesced into an adherent, finely crystalline film of grey selenium. The thickness of this film increased with time until the gaseous contents of the bulb were completely shielded from light. In spite of this, the course of the reaction seemed unaffected. The selenium seemed, in fact, to behave as if it were transparent.

Since in this reaction, selenium is the only new substance produced, it would appear that the initial phase of rate increase is to be explained in terms of autocatalysis by selenium. This is confirmed by further experiments which were carried out using a predeposited film of selenium formed in a previous run. In these, the full reaction rate was immediately established on irradiation (Fig. 1, Curve 2). In one case, a small aperture was made in the selenium deposit, well within the region of illumination. Fresh selenium was deposited only at the edges of the aperture, which remained perfectly clear while very slowly growing smaller.

FIG. 1.



An attempt was made to examine the reaction under conditions where the deposition of selenium would not exclude light from the reaction bulb. For this purpose, the liquid water was kept in a small pool in the lower part of the bulb by means of an externally applied cooling tank. After prolonged illumination, a small amount of red selenium had formed at the bottom of the water pool, but the pressure decrease was negligible. On cutting off the supply of cooling water to the tank and allowing the water in the reaction system to take up its normal position at the top of the bulb, coincident with the area at which light entered, the reaction started and followed a normal course. It was concluded that gaseous oxygen must have access to the deposited selenium for the oxidation to proceed with any appreciable speed.

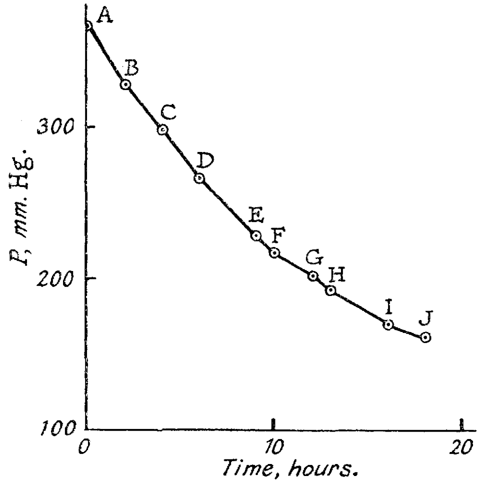
Observations on the effect of wave-length of incident light on rate of oxidation, which are summarised in Fig. 2, show clearly that light of wave-length as long as 5790 A. is completely effective in promoting reaction. The lower limit of light absorption by gaseous hydrogen selenide lies at 3200 A. (Goodeve and Stein, *loc. cit.*) and the absorption in oxygen-free aqueous solution is not substantially different (Fig. 3 : it may be noted that the molecular extinction coefficients at 3000 A. are *ca.* 5·4 and 11·0 for the gas and the solution, respectively). These results, combined with the previous observations, strongly suggest that the primary act in this reaction is absorption of light by elementary selenium. Subsequent stages clearly involve some entities which exist in an aqueous solution of hydrogen selenide but not in the gas. The values of the dissociation constants of the hydride in aqueous solution are $K_1 = 1{\cdot}30 \times 10^{-4}$ and $K_2 = 1 \times 10^{-10}$ (Hagisawa, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1941, **20**, 384), which indicate that it is possible for hydroselenide ions or hydrogen ions, or both, to fill this rôle. This is not inconsistent with the results of preliminary measurements of reaction rates, which, except for mixtures containing large excess of hydrogen selenide, fit the equation

$$dx/dt = k(a - x)^{1/2} \, . \, (b - \tfrac{1}{2}x)$$

where a and b are the numbers of moles of hydrogen selenide and oxygen, respectively, present at the start and x is the number of moles of hydrogen selenide oxidised in a time t.

Values of velocity constants in six experiments at constant light flux are 0·0054, 0·0059, 0·0077, 0·0060, 0·0063, 0·0053 mm.$^{-1/2}$ hrs.$^{-1}$; these are substantially constant. Owing to the heterogeneous nature of the system, however, modifications of technique have been found necessary for the detailed kinetic study now in hand.

FIG. 2.



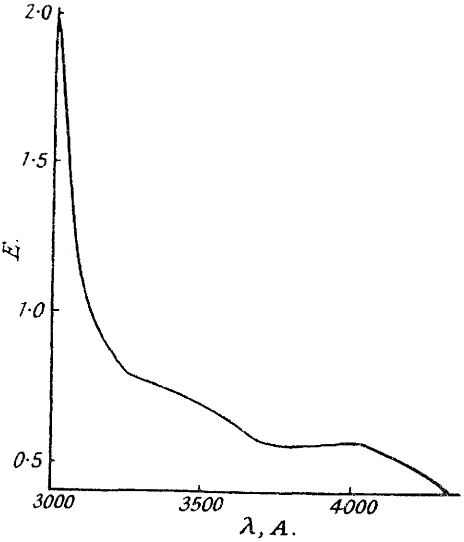
Init. P_{O_2} = 148·5 mm. Hg.
,, P_{H_2Se} = 201·0 ,,

(*Liquid water present.*)

Periods of illumination with unfiltered light from mercury arc, AB; CD; EF; GH; IJ.

Periods of illumination with filtered light from mercury arc, BC, 3650, 3663 A.; *DE,* >3663 A.; *FG,* 5790, 5777 A.; *HI,* 5461 A.

FIG. 3.



Light absorption of H_2Se *in aqueous solution.*

$E = \log_{10} I_0/I$; *cell length* = 2·0 *cm.*
$\epsilon = E/cl.$
c = *concn. in g.-mols./l.*
l = *cell length in cm.*

EXPERIMENTAL.

Preparation of Hydrogen Selenide.—Hydrogen selenide was generated by treating aluminium selenide with 1N-hydrochloric acid in a nitrogen-filled apparatus. The gas was dried over calcium chloride and phosphoric oxide and collected in a trap at − 80°. This trap was then connected to the main apparatus and pumped out while at − 80° to remove permanent gas. The hydrogen selenide was then evaporated into a previously evacuated 3-l. Pyrex flask which served as a storage vessel.

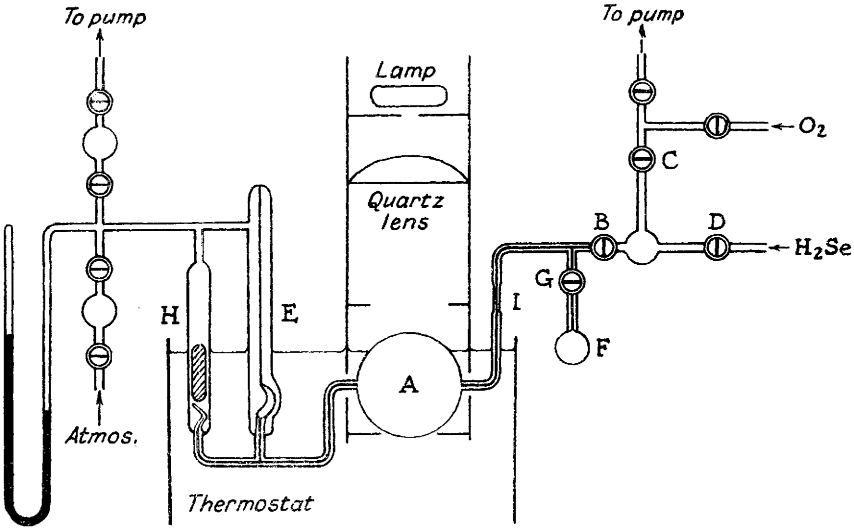
Apparatus.—The reaction was allowed to take place in a spherical Pyrex bulb, *A*, Fig. 4, of approximately 150 c.c. capacity, held in a tubular optical bench which also carried the light source and optical system. One lead from this bulb led to the tap system *BCD*, suitable manipulation of which allowed controlled pressures of oxygen and hydrogen selenide to be metered into the bulb. Another lead connected the bulb to a Pyrex spoon-gauge, *E*, which isolated the reaction mixtures from the mercury manometer. This manometer was fitted with a glass scale and rising meniscus device, which enabled readings to be taken to an accuracy of ± 0·1 mm. Hg. The leads were made of 1 mm.-bore capillary tubing, and the dead space in the reaction system was kept to a minimum.

Temperature control of the spoon-gauge and reaction bulb was maintained by a water-filled thermostat, the temperature of which was reproducible to ± 0·005°. All the observations described here were made at 25°. To provide the gentle local cooling required to position the films of liquid water, the reaction bulb was only seven-eighths immersed in the water of the thermostat. The projecting portion was, however, carefully protected from draughts by means of a metal screen which formed part of the optical bench; with this arrangement a change in room temperature of 8° had no detectable effect on the pressure within the bulb when this was filled with an inert gas mixture to a pressure of 500 mm. Hg.

The light source consisted of a 125-watt Osira mercury vapour lamp with the outer glass sheath removed. No exact relationship could be established between the light output of the lamp and its power dissipation. However, it was found that the light output, as measured by a uranyl oxalate actinometer (Forbes and Heidt, *J. Amer. Chem. Soc.*, 1934, **56**, 2384), remained constant to ± 2% provided that the voltage drop across and the current through the lamp were kept at fixed values.

The experimental procedure was as follows. The whole apparatus was pumped to a hard vacuum, a previously weighed quantity of water in the bulb *F* being frozen at − 80°. The water was then melted and completely distilled into the reaction bulb by locally cooling this with solid carbon dioxide. Tap *G* was then closed, the reaction vessel allowed to reach thermal equilibrium with the bath, and the pressure of water vapour measured. Next, hydrogen selenide from the storage bulb was metered in to a desired pressure through the tap system *BCD*. Consideration of the solubility in water of hydrogen selenide, 0·08415 mol./l. at 760 mm. Hg and 25° (McAmis and Felsing, *ibid.*, 1925, **47**, 2633), and the volumes of water taken, usually about 0·2 c.c., relative to the volume of the reaction vessel, shows that this method gives rise to little error in the measurement of the pressure of hydrogen selenide. Then, with tap *B* closed, the portion of the apparatus between *BC* and *D*, which acts as a gas pipette, was thoroughly evacuated to remove hydrogen selenide, and oxygen pipetted into the reaction vessel. Immediately after the admittance of oxygen, the capillary constriction *I* was sealed by means of a small blowpipe flame. This operation gave rise to practically no pyrolysis of the hydride if carried out before back diffusion along the capillary occurred. The total pressure in the reaction vessel was then measured. The preparations were then complete, the reaction mixture, of known composition being contained in a completely sealed, all-glass enclosure, the pressure within the enclosure being susceptible of measurement at any time by means of the spoon gauge and manometer.

FIG. 4.



At the end of the experiment, to preserve the spoon from destruction, communication between the spoon and its envelope could be re-established by breaking the capillary seal in *H* with a magnetic hammer.

The authors wish to express their gratitude to Dr. A. E. Braude for the light-absorption measurements made on aqueous solutions of hydrogen selenide.

BIRKBECK COLLEGE, E.C. 4.

[*Received, June 5th*, 1947.]