388. *The Photochemistry of Selenium. Part II. The Kinetics of the Oxidation of Hydrogen Selenide.*

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Kinetic measurements have been made on the photochemical oxidation of hydrogen selenide in the presence of liquid water and selenium. The reason is shown to be of the first order with respect to oxygen and of half order with respect to hydrogen selenide, and the reaction rates to be dependent on only some small fractional power of the light intensity. A suggestion is made regarding the mechanism of this reaction.

A QUALITATIVE description of the reaction between oxygen and hydrogen selenide was given in Part I of this series (Ives and Pittman, *J.*, 1948, 766). It was shown that, for oxidation to occur, the presence of selenium and water were necessary and that reaction was promoted by light in the near ultra-violet and visible regions. This paper describes a quantitative investigation of the same system.

It is surprising, in view of the heterogeneity of the reaction system, that the kinetics have proved to be simple, and the results, which are self-consistent and reproducible, suggest a novel explanation of the reaction mechanism.

The apparatus used was similar to that described in Part I. The dependence of reaction rate on pressures of reactants was studied in a series of isolation experiments in which an attempt was made to measure instantaneous rates at arbitrary fixed pressures of one or other of the reactants. The procedure adopted was to admit oxygen and hydrogen selenide to the reaction bulb, which already contained water and a preformed film of selenium, to pressures in slight excess of those at which the rate was to be determined. This excess was so estimated that the required pressure conditions were attained after, say, 1½ hours of illumination. The reaction vessel was then alternately illuminated and darkened for periods of one hour until the desired pressure was adequately " bracketed." The total pressure within the vessel was measured at the beginning and end of each hour of illumination, and the observed pressure decrement was assumed to be approximately equal to the instantaneous rate corresponding to the mean pressures of reactants obtaining over that hour. These rates were then plotted against the products $P_{O_2}P_{H_2Se}^{\frac{1}{2}}$, P_{O_2} and P_{H_2Se} being respectively the mean pressures of oxygen and hydrogen selenide just mentioned. The instantaneous rate, under the desired conditions of pressure, was then obtained from this plot by interpolation. The rates given by this method for predetermined pressures of reactants are shown in Figs. 1 and 2 (and in Table I), in which reaction rate is plotted against the half-power of the pressure of hydrogen selenide at constant oxygen pressure and the first power of the pressure of oxygen at constant pressure of hydrogen selenide.

These results leave no doubt that the following rate equation may be written:

$$\mathrm{d}(P_{H_2Se})/\mathrm{d}t = k(P_{H_2Se})^{\frac{1}{2}}.(P_{O_2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In a continuous reaction the rate may be defined by the equation:

$$\mathrm{d}x/\mathrm{d}t = k(a - x)^{\frac{1}{2}}.(b - \tfrac{1}{2}x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where *a* and *b* are the number of moles of hydrogen selenide and oxygen, respectively, initially present in the reaction vessel, and x is the number of moles of hydrogen selenide oxidised in a time t. For the case in which oxygen is in excess, this gives on integration and substitution :

$$t = -\frac{4}{k2(P^{i}_{O_2} - \frac{1}{2}P^{i}_{H_2Se})}\tan^{-1}\frac{P_{H_2Se}}{2(P^{i}_{O_2} - \frac{1}{2}P_{H_2Se})}$$

where P^{i} refers to initial pressures and P to pressures at a time t. k can therefore be evaluated by plotting the variable part of this equation against time. This method was used in the preliminary kinetic investigation reported in Part I. The results obtained were not, however, completely satisfactory, for the curves, though linear over the first parts of the experiments, showed an increase of gradient towards the ends. Also, though it is not rendered markedly apparent by this method of plotting, it was observed that the rates showed considerable periodic variation in time.

FIG. 1.

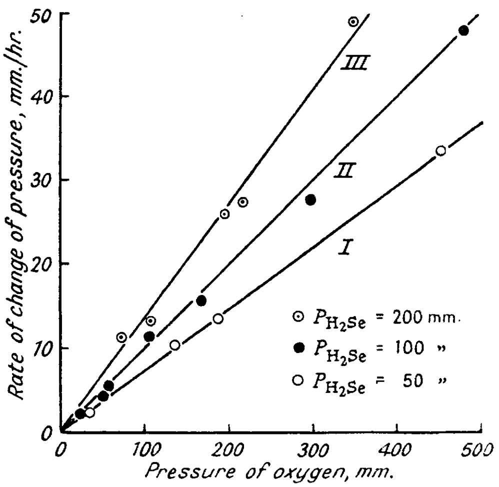


FIG. 2.

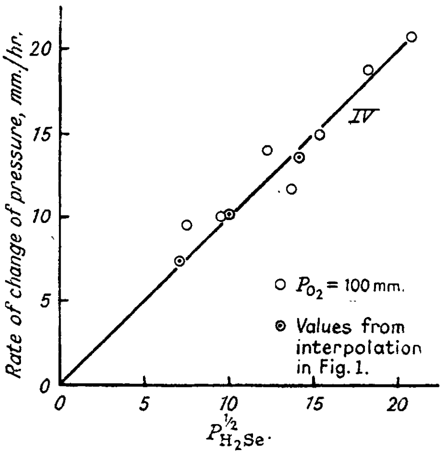


TABLE I.

Pressure of H_2Se = 50·0 mm. Fig. 1, Curve I.

P_{O_2}, mm.	35·0	135·2	187·2	450·0
dP/dt, mm./hr.	2·3	10·4	13·5	33·6

Slope Curve I = m_1 = 7·4 × 10^{-2}. $k = \frac{2}{3}m_1/50^{\frac{1}{2}} = 7·0 \times 10^{-3}$.

Pressure of H_2Se = 100·0 mm. Fig. 1. Curve II.

P_{O_2}, mm.	22·5	50·6	57·5	59·7	105·0	160·7	296·3	474·3
dP/dt, mm./hr.	2·1	4·3	5·6	5·8	11·4	15·8	27·8	48·0

Slope Curve II = m_2 = 10·1 × 10^{-2}. $k = \frac{2}{3}m_2/100^{\frac{1}{2}} = 6·8 \times 10^{-3}$.

Pressure of H_2Se = 200·0 mm. Fig. 1. Curve III.

P_{O_2}, mm.	73·0	108·0	193·3	214·8	346·9
dP/dt, mm./hr.	11·3	13·2	26·0	27·4	49·0

Slope Curve III = m_3 = 13·7 × 10^{-2}. $k = \frac{2}{3}m_3/200^{\frac{1}{2}} = 6·4 \times 10^{-3}$.

Pressure of O_2 = 100·0 mm. Fig. 2. Curve IV.

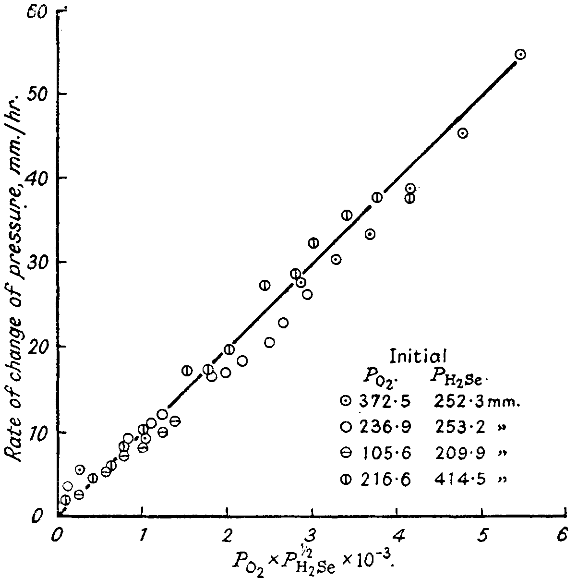
P_{H_2Se}, mm.	431·3	333·0	238·3	147·3	185·0	90·0	57·3
dP/dt, mm./hr.	20·8	18·3	15·4	12·1	13·6	9·5	7·6

Slope Curve IV = m_4 = 1·0. $k = \frac{2}{3}m_4/100 = 6·7 \times 10^{-3}$.

It was found that much more consistent readings could be made if the experiments were carried out under intermittent illumination, the reaction vessel being illuminated and darkened for alternate periods of one hour. The resulting pressure variations could not easily be examined by plotting the relevant quantity from the integrated rate equation against time. The average rates of change of pressure over the periods of illumination were, therefore, plotted against the products of the mean pressures of oxygen and the square roots of the mean pressures of hydrogen selenide obtaining over those periods, in a manner similar to that used in the analysis of the measurements made in the isolation experiments. The results of four typical experiments plotted in this way are shown in Fig. 3. The slope of this curve is readily seen to be equal to $\frac{3}{2}k$ and, as its numerical value is $1{\cdot}0 \times 10^2$, the average value of k for the four runs is $6{\cdot}7 \times 10^{-3}$ mm.$^{-\frac{1}{2}}$ hr.$^{-1}$.

The agreement between the various values of k, including those reported in Part I, seems highly satisfactory, particularly as many different selenium films were used over the course of the work. In general, any particular film was used only for three runs, except in the early part of the investigation where sufficient experiments were made, using the same film, to establish that the catalytic activity of the film remained sensibly constant after a minimum thickness had been reached.

FIG. 3.



It might also be pointed out that the increase in the value of k, found in experiments performed under continuous illumination, was not due to a permanent increase in catalytic activity of the selenium film, since values of k for the initial stages of consecutive experiments with the same film were approximately equal. It seemed to arise from some effect which was cumulative in continuous light but decayed in the dark, as is shown by the more uniform behaviour of the system in intermittent light. The behaviour of the system in darkness provides further evidence on this point. In all cases slow reaction occurred in the dark. No correlation between the rate of this dark reaction and corresponding rates under illumination could be established; the relation appeared to depend more on the previous history of the system than on the concentrations of the reactants. However, if this dark rate was measured over a series of short intervals of time subsequent to the shutting off of light from the reaction vessel, it was found to decay rapidly, falling in the course of thirty minutes to about one-third of its initial value and then becoming constant. Such behaviour could be explained by an accumulation of some intermediate product, *e.g.*, selenium dioxide or hydrogen perselenide (cf. Neilsen *et al.*, *J. Amer. Chem. Soc.*, **1939**, **61**, 440), which undergoes further reaction. This however seems unlikely, as no pressure changes were observed when oxygen or hydrogen selenide alone was exposed to light, in the presence of selenium and water, for long periods.

It was shown in Part I that the rate of oxidation depended little upon the wave-length of incident light over the range examined, and because of the experimental conditions it followed that the reaction rate could only vary as some small fractional power of the light intensity. This conclusion was confirmed by further experiments. In these, the reaction vessel was illuminated with filtered light (5790, 5777 A.), relative intensities being measured with a selenium photocell of reasonably linear response in this spectral region. A comparison of the relative rates and relative light intensities is made in Table II.

TABLE II.

Mean P_{O_2}, mm.	Mean P_{H_2Se}, mm.	Rel. light intensity.	dP/dt, mm./hr.
218·6	255·4	100	27·2
215·7	249·7	28	21·4
213·1	244·6	100	26·0
208·4	235·1	44	19·6
205·9	230·2	100	24·0
203·6	225·5	10	16·9
201·4	221·1	100	20·4

Discussion.

It was suggested in Part I that the primary act in this reaction is the absorption of light by selenium and that subsequent stages involve hydroselenide ions or hydrogen ions or both. These entities cannot be concerned in the primary act as there is no light absorption in the visible region by oxygen-free solutions of hydrogen selenide, whereas light of wave-length as long as 5790 A. is effective in promoting oxidation.

The appearance of the square root of the pressure of hydrogen selenide as a term in the kinetic equation may be adduced as evidence for the participation of the products of electrolytic dissociation in the reaction. For example, if the concentration of hydroselenide ions is rate controlling and the hydride behaves as a weak electrolyte, then

$$[HSe^-] = (K_1 . [H_2Se])^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where K_1 is the first dissociation constant of the hydride. This can be rewritten as

$$[HSe^-] = (K_1 k P_{H_2Se})^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where P_{H_2Se} is the pressure of hydrogen selenide in the gaseous phase and k is a partition coefficient.

When the photoelectric properties of selenium are considered, the possibility arises that some process analogous to electrolysis might occur with the consequent production of uncharged radicals and that it might be these which undergo oxidation. The system would then act as a photo-galvanic cell. Such cells are not novel (cf. Sabine, *Nature*, 1878, **17**, 512; Minchin, *Proc. Roy. Soc.*, 1895, **58**, 142; Ries, " Das Selen," 1918, J. C. Hubers; von Hippel *et al.*, *J. appl. Physics*, 1946, **17**, 215). von Hippel *et al.* made a cell in which a metal electrode, coated with selenium was immersed in a solution of selenious acid containing a second electrode of a noble metal or a second selenium-coated plate. A polarising voltage of the order of two volts was used, the auxiliary electrode being made the anode. They found that the current generated in such cells was proportional to the intensity of incident light when sufficient polarising voltage was applied, but, when this voltage was decreased, the linearity failed at low intensities, whilst at greater intensities the current became practically constant and independent of light intensity. The electrode processes suggested in this work are :

Cathode (illuminated) $\quad H_2SeO_3 + 4e^- + 4H^+ = Se + 3H_2O$
Anode (Se) $\quad Se + 3H_2O = H_2SeO_3 + 4e^- + 4H^+$

It is also pointed out that if other electrolytes were used, *e.g.*, hydrochloric acid, the selenium on the illuminated electrode was stripped off on continued use.

The preliminary working hypothesis that the oxidation under investigation proceeds *via* an electrolytic process, though fitting our observations in a general way, requires elaboration to explain fully the kinetics of the reaction.

A mechanism which seems to account for the observed characteristics is now proposed.

Let it be assumed that the electrons within a crystal of selenium possess a limited power of circulation within the crystal lattice, but that the average density of electrons surrounding the nuclei in the bulk of the lattice must remain fixed. This implies that, owing to dissymmetry at the surface of the crystal, a potential barrier will exist there, preventing the flow of electrons to or from the crystal. This is consistent with the observations of Brown (*Phil. Mag.*, 1914, [vi], **28**, 496) who showed that, when a crystal of selenium was illuminated at certain points, the conductance of the whole crystal was increased, and with the fact that photoelectrons are not emitted from selenium at wave-lengths greater than 2200 A. (Hughes, *Phil. Trans.*, 1912, **212**, *A*, 205).

Consider, then, a film of selenium immersed in a solution of hydrogen selenide in darkness. Let one face of the film be illuminated. Absorption of radiation will decrease the electron affinity of the surface layer of selenium, and the relative changes of electron affinity with respect to the two ionic species in solution will result in an increased field of force between the hydrogen ions and the face and a decreased field of force between the negative hydroselenide ions and the face. Hydrogen ions will thus become preferentially adsorbed. This circumstance would facilitate the transfer of electrons across the potential barrier and it might be expected that some adsorbed hydrogen ions would be discharged. However, there is no evidence for the production of hydrogen in any of these experiments. In most cases oxidation was carried to completion, and the pressure decrements were found to fit the stoicheiometric requirements of simple oxidation.

An explanation of this can be given as follows. Imagine a hydrogen ion adsorbed at the light face. Owing to the modification by illumination of the potential barrier at this surface an electron is capable of leaving the selenium lattice and discharging this ion, the positive charge produced on the selenium atom adjacent to this former ion being neutralised by a general electron drift towards the light face. What is virtually a hydroselenide radical is formed and this remains incorporated in the lattice structure. Such a system is unstable and a further transfer of an electron to the hydroselenide radical occurs. The increase in volume of the radical on the acquisition of negative charge renders its position in the lattice geometrically untenable and it is expelled as a hydroselenide ion. This does not, however, leave the surface but remains adsorbed there, thus binding one of the two excess positive charges now present on the selenium lattice and forming part of an electrical double layer. The local excess of positive charge on the lattice due to this double layer causes a migration of the second positive charge to regions of lower potential energy—a process reminiscent of the drift of positive " holes " to the dark side of a selenium crystal, so frequently postulated in the discussion of barrier-layer cells.

These ideas may be further expanded. The system consisting of illuminated selenium in contact with an aqueous solution of hydrogen selenide may be considered as a reversible electrode at which an equilibrium, $Se + H^+ + 2e^- \rightleftharpoons HSe^-$, can be established, thus giving rise to a potential

$$E = E_0 + (\boldsymbol{R}T/2\boldsymbol{F}) \ln [H^+]/[HSe^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $[H^+]$ and $HSe^-]$ are the respective concentrations of hydrogen ions and hydroselenide ions in the solution. E_0 will depend, in some way, on the state of illumination of the system and, as this was kept constant in all the kinetic experiments, E_0 will be constant; also $[H^+] = [HSe^-]$, and therefore E will be constant.

In the establishment of this equilibrium, hydrogen ions will be discharged and hydroselenide ions generated; there will thus be an excess of hydroselenide ions over the demands of electroneutrality, and there will be a migration of positive charge to the dark face, the number of positive charges migrating being equal to the number of hydroselenide ions produced. Hydroselenide ions will therefore become adsorbed at the dark face, forming a double layer at this site. The total number of ions so adsorbed can be calculated as follows.

Let the double layer at the light face possess a fixed electrical capacity C. This assumption is justifiable, since this capacity will be proportional to some function of the light intensity and to the projected area of the illuminated surface, normal to the light beam, both of which were kept constant. The quantity of positive charge produced at this face in the attainment of its equilibrium potential will then be equal to $2E'C$, where E' is the potential across the double layer, which is fixed by the equilibrium potential of the surface. Of this charge, a quantity $E'C$ will migrate to the dark side, and, to a first approximation, $E'C/q$ hydroselenide ions will become adsorbed there, q being the charge on one hydroselenide ion. It should be noted that the number of ions thus adsorbed depends on the conditions at the light face and is in no way a function of the area of the dark face.

Now the ions adsorbed at the dark surface will be in equilibrium with those in the bulk of the solution which possess energy of thermal motion; therefore the distribution of ions between the two phases can be described by the equation

$$n = \text{const.}\ [c_{\text{sol}} \,.\, \exp(x/RT)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where n = number of HSe^- ions in the adsorbed layer, c_{sol} = concentration of HSe^- ions in solution, x = the energy of binding of one g.-ion of HSe^- ions in the double layer, and R and T have their usual significance.

The binding force, P, between charges in the double layer will be defined by $P = q^2/r^2D$, where q = ionic charge of HSe^-, r = distance of separation of charges in the double layer, and D = a quantity of the nature of dielectric constant.

Thus it may be assumed, as an approximation, that P is constant; it follows that x is constant, and from equation (4) we can write

$$\ln n = \ln c_{\mathrm{sol}} + \text{constant}$$

or

$$n = c_{\mathrm{sol}} \, . \, \text{constant}$$

Consider now the behaviour of such a system towards oxygen. The free hydroselenide ions in solution will not undergo oxidation as no electron acceptor is available, but, if the energy of the electrons produced by oxidation is sufficient to enable them to cross the energy hump on the dark side, oxidation will proceed at this site. Comparison of the free energy change involved in the reaction

$$2\mathrm{HSe}^- + \tfrac{1}{2}\mathrm{O}_2 = \mathrm{H}_2\mathrm{O} + 2\mathrm{Se} + 2e^-$$

with that of the discharge of hydroselenide ions, indicates that such a potential barrier might act as a discriminating filter between the electrons produced by these two reactions.

It will be seen that the adsorption equilibrium, previously discussed, will remain sensibly unaffected by the reaction proceeding at the dark face. The oxidation does in effect give rise to an electric current flowing between the light and dark faces of the selenium, the circuit outside the selenium layer being completed by the solution. If there is no accumulation of charge at any point in this circuit, which is unlikely if transport effects are ignored, then the existing electrical tensions should remain unchanged and adsorption defects arising from the oxidation should become repaired by the forced diffusion of ions.

This may be restated in a different way. The removal of hydroselenide ions from the dark face by oxidation is equivalent to the removal of positive charge from the selenium layer as a whole, and the potential of the light face will therefore fall. To restore the equilibrium potential defined by equation (3), hydrogen ions will be adsorbed and discharged at this face, as already described, with a consequent reinstatement of the electrical and adsorption conditions previous to the oxidation. This process will be a continuous one, and as oxidation proceeds selenium will actually be dissolved from the light face. For every selenium atom so removed, two selenium atoms will be deposited at the dark side. This gives an explanation of the observations regarding the " dissolution " and " reprecipitation " of selenium noted in Part I. It is understandable that the red modification, which is the least stable, should be first to suffer attack. The stripping of selenium from the cathodes of von Hippel's cells might also be recalled and it can be added that the selenium deposit produced over the course of several experiments always showed considerable etching in the illuminated area.

If this is an adequate description of the mechanism of the oxidation, and if the simplifying assumptions are made that the reaction is of the first order with respect to oxygen and that the system is in continuous equilibrium, then the rate of oxidation can be defined by the expression

$$\text{rate} = k \, . \, [\mathrm{HSe}^-] \, . \, P_{\mathrm{O}_2}$$

which is in agreement with experiment.

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