# LXXXI.—*The Budde Effect in Bromine. Part I. The Photoactive Constituent of Wet Bromine.*

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THE experiments of Dixon and of Baker (*Rep. Brit. Assoc.*, 1894, p. 493; J., 1884, **45**, 611) on the influence of small traces of water on physical and chemical changes have led to the theory of internal equilibrium of Smits ("The Theory of Allotropy," Longmans and Co.) in which it is assumed that water acts as a catalyst in accelerating the attainment of equilibrium between various polymeric or allotropic forms of simple molecules in homogeneous systems which were originally in metastable states. To exert this catalytic activity it must be assumed that the water makes a temporary complex with the reactant, which complex must be capable of excitation or activation more readily than the reactant molecules themselves.

The earlier experiments of Budde (*Pogg. Ann.*, 1871, **144**, 213; *Wied. Ann.*, 1879, **6**, 477), Mellor (J., 1902, **81**, 1280), and Bevan (*Phil. Trans.*, 1903, **202**, *A*, 71) as well as those of Pringsheim (*Wied, Ann.*, 1887, **32**, 385), Richardson (*Rep. Brit. Assoc.*, 1888, p. 89). Shenstone (J., 1897, **71**, 471), and Cordier (*Monatsh.*, 1900, **21**, 660) revealed the fact that dry chlorine differed from moist chlorine in that on exposure to radiation, especially in the blue and violet portion of the spectrum, moist chlorine underwent expansion, but dry chlorine, although absorbing the radiation, showed no such expansion. This "Budde" effect has likewise been noted by Budde (*loc. cit.*) and by Ludlam (*Proc. Roy. Soc. Edinburgh*, 1924, **44**, 197) in the case of bromine.

The early experiments made it clear that the expansion in the moist halogen was due to the conversion of absorbed radiation into thermal energy of molecular agitation and it was assumed from this fact that, since the Budde effect is still obtainable in a region of the spectrum in which the quantum is small (in the case of bromine a Budde expansion is still noticeable at $\lambda = 5800$ Å., whilst according to Franck [Photochemical meeting, Oxford, 1925], from a consideration of the distribution of the absorbed energy between rotational, oscillatory, and electronic quantum states of the molecule, dissociation of the molecule cannot be effected with a wavelength greater than $\lambda = 5000$ Å.), the thermal effects are not produced by a primary activation of a bromine molecule followed by a splitting into atoms with their subsequent recombination. It has also been shown by Sir J. J. Thomson (*Proc. Camb. Phil. Soc.*, 1901, **11**, 90) that the formation of charged ions according to the reaction $Br_2 \rightleftharpoons Br^{\bullet} + Br'$ does not occur, a view which can likewise be demonstrated to be improbable from a comparison of the magnitudes of the energies required for dissociation into atoms and ions respectively. How the moisture caused the conversion of radiant into kinetic energy was not elucidated. We may note, however, that Bevan (*loc. cit.*) postulated the existence of complexes such as $(Cl_2)_x(H_2O)_y(H_2)_z$ in the water-sensitised hydrogen–chlorine mixture, and on analogy with this conception it might be argued that a hydrate $(Br_2)_x(H_2O)_y$ was the photoactive constituent responsible for the Budde effect. Alternatively it might be suggested that in the metastable, freshly distilled, dry halogen a photosensitive polymeride of bromine is absent, but is present when the inner equilibrium is attained with the aid of the catalytic water. With the exception of the work of Coehn and Jung (*Z. physikal. Chem.*, 1924, **110**, 705) on the hydrogen–chlorine reaction, no quantitative work on the influence of water on such reactions has been accomplished and it appeared of interest to examine the Budde effect in bromine in more detail.

It may be stated at the outset that the experimental data support the hypothesis that the Budde effect is due to a photosensitive bromine hydrate of composition $Br_2,H_2O$ and that the water does not function as a catalyst in the formation of a photosensitive polymeride of bromine. Having established this point, it was necessary to investigate the properties of this hydrate in more detail such as its heat of formation, the value of the equilibrium constant of the reaction $Br_2 + H_2O \rightleftharpoons H_2O,Br_2$ and the distribution of the hydrate, *i.e.*, the partition of the hydrate between the surface and bulk phases in the reaction vessel.

Finally, it was decided to investigate how far the absorption spectrum of the hydrate differed from that of bromine vapour, to evaluate its absorption coefficient, and to suggest a hypothesis as to the mechanism of operation of the Budde effect.

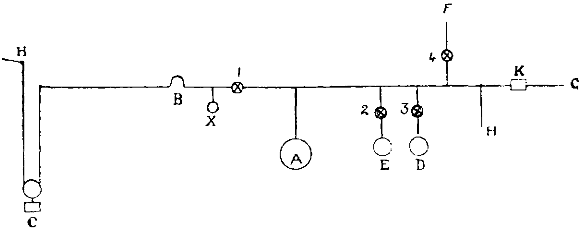
The importance of these points would appear not to be confined to the Budde effect alone, for if hydrates do exist in the gas or liquid phases of non-polar, or feebly polar substances, it is to be anticipated that the walls of the containing vessel which adsorb water readily will likewise adsorb the hydrate. Thus the partition of the hydrate between the bulk and surface phases will obey an equation of the type found to hold in the isothermal adsorption of vapours and will prove an important factor in the relative rates at which reactions, which are *ex hypothesi* due to this hydrate, occur in the two phases.

Again, whilst dry bromine does absorb light within a large portion of the spectral region which causes the Budde effect in wet bromine, no thermal effects are to be noted. It follows that the apparent absorption is fictitious, for the light must be re-emitted as fluorescent light or scattered from the molecules. The hydrate molecules, on the other hand, absorb the light which is subsequently converted into thermal energy. The data from absorption spectra clearly do not distinguish between these two phenomena. The influence of water in cutting down the fluorescence of dry hydrogen and oxygen exposed to illumination of a quartz mercury vapour light recently noted by Baker* (J., 1925, **127**, 1990) and the fluorescence of dry active hydrogen yielding the line λ = 3064 Å., a water vapour line (Bonhoeffer, *Z. physikal. Chem.*, 1925, **116**, 39), would appear to be a phenomenon similar to that occurring in bromine.

## EXPERIMENTAL.

Two forms of apparatus were employed for determination of the effect of alteration in the partial pressures of the bromine and water on the magnitude of the Budde effect. For low partial pressures of water, the following method was devised. The reaction vessel, *A*, of 20 c.c. capacity, consisted of a bulb with plane-parallel sides, 2·35 cm. apart, connected on one side by capillary glass tubing to the phosphoric oxide tube, *X*, and the glass gauge, *B*. On the other side capillary connexions were made to the bromine and water reservoirs *D* and *E*, the drying train, *F*, the McLeod gauge, *H*, and mercury vapour pump line, *G*.

FIG. 1.



During evacuation of the reaction vessel the gauges and reactant

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* Communicated at a meeting of the Society.

reservoirs were temporarily disconnected by capillary glass inner seals 1, 2, 3, 4, which were provided with iron rods enclosed in glass permitting of fracture of the seals with the aid of an electromagnet. Between the diffusion pumps, *G*, and the apparatus a liquid air-trap was placed to prevent back-diffusion of mercury vapour. The gauge, *B*, consisted of a well-annealed (5 months), collapsed elliptical glass bulb forming a Bourdon indicator, attached to a 30 cm. glass pointer, to the end of which one arm of a quartz bifilar suspension for a mirror, *C*, was attached. The mirror was steadied by means of a mica vane dipping in water, the surface tension of which was lowered by the addition of a drop of oleic acid, thus permitting unhindered movement of the mirror. A spot of light from the mirror on a scale one metre away was followed. The sensitivity of the gauge could be varied by alteration, with the aid of a micrometer screw, of the position of the left arm, *H*, of the bifilar suspension; pressure changes of 1/120 mm. of mercury could be registered when it was in most sensitive adjustment. The gauge was calibrated with the aid of a mercury manometer and eye-piece, frequent calibration showing but little change in the characteristics.

The apparatus employed for the higher vapour pressures of water was similar to that described above, but in place of internal seals, stopcocks, lubricated by two rims of chlorinated odourless wax, were employed. In place of the water reservoir, a bulb containing sodium sulphate decahydrate was employed as source of water vapour, which was connected to the reaction vessel and pump through a small dosing apparatus of 0·3 c.c. capacity permitting of admission of small quantities of water vapour to the dry bromine. The source of light was a 1000 c.p. point light, parallel rays being obtained with a collimator, the reaction vessel being mounted in a plane-sided trough through which water was circulated from a thermostat. Between the collimator and the trough was placed a smaller trough in which the requisite colour filters could be placed.

*Materials.*—The bromine was prepared by distillation of the purest obtainable bromine, twice over zinc oxide and once over freshly prepared phosphoric oxide in a closed system which had originally been baked out. The bromine was stored over phosphoric oxide in a sealed vessel and was not used for the dry experiments until 9 months later. The data of Ramsay and Young (J., 1886, **49**, 453) were employed for the vapour pressure at various temperatures.

The sodium sulphate decahydrate was prepared by triple crystallisation and partial desiccation. The dissociation vapour pressure at 0° employed was 2·77 mm., from the value given by Baxter and Lansing in the Landolt–Bornstein tables.

The water employed was pure conductivity water, and the vapour pressures were calculated with the aid of the equation of Nernst (*Verh. deut. physikal. Ges.*, 1907, **11**, 313) : $\log_{10} P_{\text{mm.}} = -\frac{2611}{T} + 1{\cdot}75 \log T - 0{\cdot}00210T + 6{\cdot}5343$, substantiated experimentally to 100° K. by S. Weber (*Communication Lab. Leyden*, 1915, **14**, 150A).

Three different vapour pressures were employed at temperatures corresponding to the freezing points of toluene, ethyl acetate and chloroform. The values are in the following table :

| Substance. | Temperature. | V. p. above the ice in mm. Hg. |
|---|---|---|
| Melting toluene | −93° | $3{\cdot}9 \times 10^{-5}$ |
| ,, ethyl acetate | −83 | $2{\cdot}3 \times 10^{-4}$ |
| ,, chloroform | −63 | $5{\cdot}3 \times 10^{-3}$ |

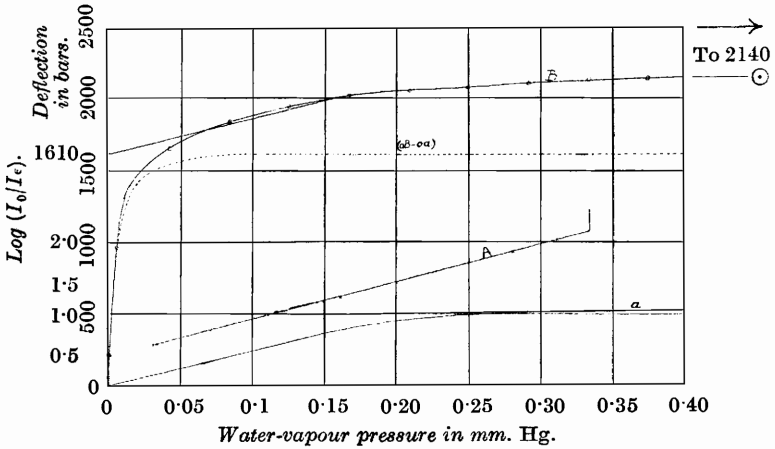
*Method of Operation.*—The method of operation employed was as follows. The reaction vessel was placed in an electric furnace and the capillaries and connexions up to the seals were wound with nichrome wire and thoroughly lagged with asbestos. One or two small parts were heated frequently with a Bunsen flame. A vacuum (less than $10^{-6}$ mm. Hg) was maintained in the system at 400° for 5 days. The seal connecting the system to the ice maintained in liquid air was first broken with the connexion still open to the pumps. The high vacuum was rapidly reached again, the pumps were disconnected, the liquid air was replaced by melting toluene, and the water vapour allowed to pass into the reaction bulb. When equilibrium was attained (over an hour), the capillary tube leading to the water-vapour container was sealed under the blow-pipe, and the reservoir removed. Dry bromine at the required partial pressure (the bromine reservoir had been previously evacuated and maintained at a desired temperature) was admitted, and the bromine reservoir removed in a similar manner. Finally, dry air was admitted to atmospheric pressure, and the connexion sealed. The phosphoric oxide tube, $X$, was sealed and the connexion to the gauge established by breaking the capillary seal (1). Finally, the tube containing the iron rod at seal (1) was sealed and removed.

The reaction vessel was brought to a uniform temperature by the circulating water, and the deflection on the gauge observed for various distances of the lamp and with various colour filters (Wratten light filters). Finally, the gauge setting was calibrated. Four separate experiments were carried out in this manner, one with dry bromine–air mixture, in which no Budde effect was noted under the most intense illumination, and three with water vapour at the partial pressures given above.

For determination of the Budde effect at higher water-vapour pressures, taps instead of internal seals were employed and evacuation was effected with a Toepler pump instead of the diffusion pumps. On admission of dry bromine and air to the reaction vessel a small Budde effect was always noticeable under strong illumination, indicating that traces of water vapour (0·001 mm.) could not be eliminated entirely by this procedure.

To admit definite quantities of water to the evacuated system, the sodium sulphate reservoir at 0° was opened to the 0·3 c.c. capillary doser, thus filling it with water vapour at a partial pressure of 2·77 mm. Bromine was admitted to the reaction vessel, and then dry air passed through the doser into the 20 c.c. bulb, thus sweeping the water vapour into the reaction system. Any number of doses could be admitted in this manner.

FIG. 2.



Neither with air nor with dry bromine on illumination was the slightest change in pressure observed, but in the presence of moisture a rapid rise in pressure, approaching an equilibrium value within 20 to 30 seconds, was always obtained. On cutting off the illumination, the light spot of the gauge indicator returned to its initial position.

An investigation of the magnitude of the Budde effect with various light filters showed (the Wratten filters 15, 16, 21, 25 as well as various combinations were permeable to photochemically active light) that light of wave-length longer than λ = 5800 Å. produced no detectable effect; light within a region 5600 Å. to 5500 Å. was particularly effective. Accordingly, a filter combination transmitting red light and light from 5400 Å. to 5700 Å.

with a maximum permeability near 5500 Å. was employed for all quantitative experiments.

An investigation revealed that the energy distribution in the various wave-lengths between 5000 Å. and 6000 Å. of the point light as measured with a thermopile and galvanometer was uniform, thus a mean of the effective extremes of the light filter could be assumed.

*Results.*—In the curve (Fig. 2) is given the relationship between the Budde effect in bars (dynes per sq. cm.) as a function of the partial pressure of the water vapour at a constant bromine pressure of 158 mm. and a temperature of 40°. Some of the values obtained, from which the curve was plotted on a very large scale so as to permit of accurate analysis, are in the following table :

Partial press. of Br, 158 mm. Temp. of bath, 40°. Distance of lamp, 15 cm.

| Press. of $H_2O$ in mm. Hg. | Deflection in bars. | Press. of $H_2O$ in mm. Hg. | Deflection in bars. |
|---|---|---|---|
| 0 | 0 | $8.3 \times 10^{-2}$ | 1830 |
| $3.9 \times 10^{-5}$ | 66 | $1.245 \times 10^{-1}$ | 1950 |
| $2.3 \times 10^{-4}$ | 226 | $1.66 \times 10^{-1}$ | 2020 |
| $5.0 \times 10^{-3}$ | 958·8 | $3.32 \times 10^{-1}$ | 2140 |
| $4.15 \times 10^{-2}$ | 1640 | $5.395 \times 10^{-1}$ | 2140 |

It will be noted that the curve may be divided into three portions; for low partial pressures of water up to 0·005 mm. the Budde effect rises rapidly; this is followed by an almost linear portion of the curve (0·03 mm. to 0·16 mm.) in which the Budde effect increases proportionally to the increase in the water-vapour pressure; finally, at high water concentrations, the Budde effect increases less rapidly, attaining a maximum of *ca.* 2140 bars at a partial pressure of 0·3320 mm., which is not affected even when the water-vapour pressure is increased to 0·5810 mm. It was suspected that this apparent maximum as well as that shown in Fig. 3 was due to complete absorption of the active radiation. Proof of the correctness of this view was obtained in the following ways. The Budde effect for these high water concentrations was found to be dependent on the distance of the source of illumination from the bulb as shown by the following data, *a* being the distance (cm.) of the lamp from the reaction vessel, and *b* the deflection in scale-divisions :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *a* ...... | 72 | 62 | 52 | 42 | 32 | 22 | 15·5 | 11 |
| *b* ...... | 5 | 7 | 10 | 16 | 25·5 | 44—45 | 82 | 160 |

It might indeed be argued that the flattening of the curve is caused by increased heat radiation outward, as the Budde effect increases. In the following manner this view was found to be incorrect, within the magnitudes of the Budde effect, and our first view more directly confirmed. A very fine platinum filament, terminating in thick platinum wires, was sealed in the reaction vessel, which was filled with bromine and water vapour to the desired partial pressures. Several partial pressures of bromine were employed. An electric current was passed through the spiral filament and from a knowledge of the current passing and the potential difference across the spiral the heat evolution in calories per second to give various expansions measured on the gauge could readily be determined. Fig. 4 shows the curve, average values of deflections for different bromine concentrations (these varied only a little) being plotted as ordinates against calories per second developed by the spiral as calculated from $H = 0{\cdot}24RI^2$. It will be observed that the curve bends only slightly within the limits employed. If, now, one takes two deflections on curve A (Fig. 3) and plots as abscissa the heat corresponding, as obtained from Fig. 4, and then from this interval one obtains the scale plotting in place of bromine pressure as abscissa, the calories per sec. (Curve C), one observes that the two curves coincide along the rectilinear portion. It is clear that if the falling off of the Budde effect were due to increased heat radiation, the two curves should coincide throughout. But the Budde effect falls off much more rapidly, supporting the view that the maximum is due to complete absorption of the actinic rays.

The following furnishes additional proof for the total extinction of the actinic rays at the maximum. When the surface is practically saturated, the course of the curve is governed by the absorption of light in accordance with Beer's law.

$$I_\epsilon = I_0 e^{-k(dc+K)}$$

where $K$ is the constant concentration of hydrate on the surface (see later, p. 593).

Hence $\log (I_\epsilon/I_0) = - k(dc + K)$ or $\log (I_0/I_\epsilon) = k'c + K'$.

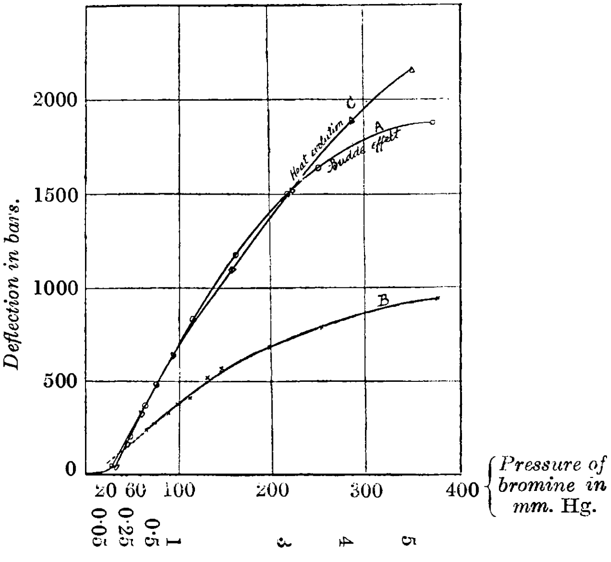
$C$, the concentration of the hydrate, is proportional to the water concentration in the bulk phase. Curve A (Fig. 2) shows that from 0·03 mm., where the surface concentration is practically up to saturation, this proportionality holds true until complete absorption of the light.

Over a certain pressure range the Budde effect increases proportionally to the increase in the partial pressure of the water vapour.

In Fig. 3 are plotted the Budde effects as functions of the partial pressures of bromine at the constant water-vapour pressures of 2·77 mm. (A) and 0·20 mm. (B), respectively, and at 40°, the distances of the lamp from the bulb being 21 and 32 cm., respectively. Above partial pressures of bromine of *ca.* 20 and 40 mm., respectively, the curves follow the same course as those noted for the constant bromine–variable water-vapour pressure curves, *viz.*, the Budde effect is proportional to both the partial pressure of the bromine and of the water vapour. Such a relationship is most readily interpreted on the assumption that the photoactive constituent responsible for the Budde effect is a bromine hydrate of composition $Br_2,H_2O$ in mass equilibrium with the reactants according to the equation

$$Br_2 + H_2O \rightleftarrows Br_2,H_2O.$$

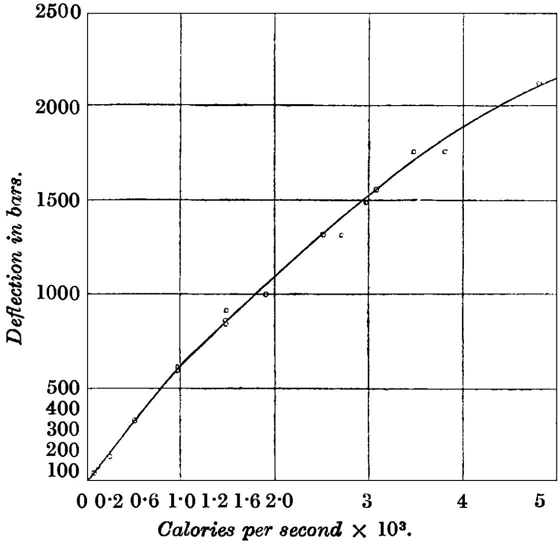
FIG. 3.



In the light of this hypothesis the convex form of the curve for low water-vapour pressure (Fig. 2) and the concave form of the constant water-vapour pressure curves at low bromine pressures (Fig. 3) are significant.

It is clear that when the partial pressures of water are low (below 0·005 mm.) the Budde effect rises more rapidly than we should be led to expect from application of the law of mass action to the bulk phase. If bromine hydrate were strongly adsorbed by the walls of the glass vessel, the surface concentration increasing with the partial pressure until a saturation maximum was attained at about 0·10 mm., the reason for this increase of the Budde effect at low partial pressures of water vapour and the convex form of the curve when the walls are dry would be clear. Again, if in the presence of high pressures of water and low partial pressures of bromine the walls of the vessel are covered with water, the Budde effect will consequently be proportional to the bromine hydrate in the gas phase at the commencement, but will rise more rapidly as the pressure of the hydrate increases and displacement of the adsorbed water by the latter commences, thus explaining the initial concave form of the curves for low bromine and high water-vapour pressures. With low partial pressures of water (Fig. 3, curve B) it will be seen that the displacement of water from the surface by the hydrate commences at a lower partial pressure. After this initial curvature the curve rises in a linear manner proportional to the quantity of bromine hydrate present both in the surface and the gas phases.

FIG. 4.



Such a view, which is advanced from a knowledge of the hygroscopic nature of glass and the convex and concave forms of the bromine–water-vapour pressure curves at low partial pressures, is greatly strengthened by careful analysis of the convex curve. The Budde effect is, according to this view, due to absorption of light by bromine hydrate which is present both in the bulk phase and on the surface of the glass. The curve at low partial pressures of water is thus the effect of both the bulk and the surface concentrations. The bulk concentration increases in a linear manner with increase in water-vapour pressure until the light absorption becomes great, and this portion contributes a Budde effect given by the line oa (Fig. 2). The surface concentration at various partial pressures contributes a Budde effect given by the curve oB—oa. If this be the case, it should be capable of expression in the form of an adsorption isotherm. Since it is probable that the water vapour and hydrate layer is but one molecule thick, the partial pressures being far lower than those employed by McHaffie and Lenher (J., 1925, **127**, 1559), where multimolecular layers were formed, the Langmuir isotherm should be applicable :

$$x = ap/(1 + bp),$$

where $x =$ the surface concentration of the hydrate or is proportional to the Budde effect in the surface, $p =$ the partial pressure of the hydrate in the gas phase or is proportional to the concentration of water, and $a$ and $b$ are constants.

The prolongation of the rectilinear portion of the curve, where the surface is hydrate-saturated, intersects the ordinate at 1610 bars. This, then, is the limit to the Budde effect produced by the surface phase.

Hence when $p$ is large, $x = a/b = 1610$,
for $p = 0{\cdot}0005$, $300 = 0{\cdot}0005a/(1 + 0{\cdot}0005b)$.
From which we obtain $b = 458$, $a = 7{\cdot}38 \times 10^5$.

The following table shows the calculated and the observed values (in bars) of the Budde effect in the surface phase for increasing water-vapour pressures.

| Partial press. of $H_2O$ (mm.). | $x$ calc. | $x$ obs. | Partial press. of $H_2O$ (mm.). | $x$ calc. | $x$ obs. |
|---|---|---|---|---|---|
| $3{\cdot}9 \times 10^{-5}$ | 28·4 | 66 | 0·01 | 1320 | 1200 |
| $2{\cdot}3 \times 10^{-4}$ | 154 | 226 | 0·03 | 1500 | 1500 |
| $5{\cdot}0 \times 10^{-4}$ | 300 | 300 | 0·08 | 1573 | 1590 |
| $5{\cdot}0 \times 10^{-3}$ | 1100 | 950 | | | |

Taking into consideration the difficulties of evaluating the actual values of the Budde effect for the initial portion of the curve, which is extremely steep, the agreement between the observed and the calculated values does not exceed the experimental error.

The bromine hydrate which is the photoactive constituent responsible for the Budde effect is thus present in the reacting system both on the walls of the containing vessel and in the homogeneous gas phase, the distribution between surface and bulk phases obeying the usual adsorption isotherm equation.

In order to confirm the view that even at low partial pressures of water vapour there was adsorbed on the walls of the containing vessel a relatively large quantity of hydrate even when the bulk concentration was low, the following experiment was devised.

A small horizontal cell 4 cm. long and 1·25 cm. in diameter with plane glass ends was constructed. Inside the cell a round coverslip was placed in a vertical plane so that the light passed through the ends of the cell and through the coverslip; a gentle shaking of the cell permitted the coverslip to fall down so that the narrow circular beam of light now passed only through the ends of the cell and the gas phase. Behind the cell a small Moll thermopile was placed so as to obtain a measure of the radiation absorbed by the cell. In addition, the cell was connected to the glass gauge and bromine reservoir in the usual manner.

The following data were obtained on illumination with light passing the colour filters employed in the previous investigation.

*Expt.* 1.

| Cell. | Gas in cell. | Thermopile galvo. deflection. | | Budde effect. |
|---|---|---|---|---|
| Coverslip up. | Air. | 22·27 | 2·04 | nil |
| ,, ,, | Bromine at 104 mm. | 20·23 | | 7—8 av. 7·5 |
| Coverslip down. | ,, ,, ,, | 21·15 | 1·12 | 4 |
| ,, ,, | Air. | 22·27 | | nil |

It will be noted that with air, the position of the coverslip did not affect the amount of light falling on the thermopile, indicating absence of scattering, reflection or absorption of the light due to the glass. When the coverslip was up, the light passed through four glass–gas interfaces and when down through but two such interfaces, the former producing a larger Budde effect and a larger light absorption. If the amount of hydrate in the homogeneous gas phase be denoted by $x$, producing a Budde effect, $kx$, and a light absorption, $lx$, and that on each glass–gas interface be denoted by $y$, producing effects $ky$ and $ly$, respectively, we obtain the following relationships:

(*a*) From the Budde effect.

$$4y + x = 7{\cdot}5k \quad \text{and} \quad 2y + x = 4k,$$

whence

$$2y = 3{\cdot}5k \quad \text{and} \quad x = 0{\cdot}5k,$$

or 12·5% of the Budde effect is produced by hydrate in the gas phase and 87·5% produced by hydrate on the two flat ends of the cylinder.

(*b*) From the absorption of light.

$$4y + x = 2{\cdot}04l \quad \text{and} \quad 2y + x = 1{\cdot}12l,$$

whence

$$2y = 0{\cdot}92l \quad \text{and} \quad x = 0{\cdot}20l,$$

or 17·8% of the Budde effect is produced by hydrate in the gas phase and 82·2% produced by hydrate on the two flat ends of the cylinder.

A repetition of this experiment with a bromine pressure of 140 mm. with the same water-vapour pressure gave the following values:

| | Coverslip up. | Coverslip down. |
|---|---|---|
| Absorption | 3·06 | 1·75 |
| Budde effect | 12 | 7 |

whence we obtain the following percentages for the distribution of the hydrate :

| | % In bulk phase. | % On surface phase. |
|---|---|---|
| From Budde effect | 28 | 72 |
| From absorption of light | 25·3 | 74·7 |

As the concentration of hydrate is increased by elevation of the bromine pressure, the bulk concentration of hydrate increases more rapidly than the surface concentration, which, as shown in the previous experiments, finally approaches a surface saturation maximum. From Fig. 2 the percentage of the maximum Budde effect caused by the surface phase is 75, and that of the volume 25 under the experimental conditions.

In Fig. 3 the initial concave portion of the curve was attributed to the effect of the surface adsorption of water vapour which when present in large quantities could displace bromine hydrate when present in but small quantities, *i.e.*, at low partial pressures of bromine.

To confirm this view, both the light absorption and the Budde effect for the bromine in the small cell were determined for low and high partial pressures of water. If excess of water displaces the adsorbed bromine hydrate from the glass surfaces, we should anticipate that, in spite of the increase of the bromine hydrate in the bulk phase due to the addition of water, the removal of the bromine hydrate by displacement from the walls will cause a diminution in the total Budde effect. The following data were obtained :

| Cell containing | Deflection for thermopile. | Budde effect. | Absorption. |
|---|---|---|---|
| Air | 25·49 | 0 | — |
| Bromine at 144 mm. | 22·49 | 11 | 3·00 |
| Bromine at 144 mm. and $H_2O$ vapour at 18° | 23·12 | 9 | 2·37 |

The diminution in the Budde effect on a very large increase in the partial pressure of water is clearly brought out.

## *Summary.*

The Budde effect in bromine is shown to be proportional to both the partial pressure of bromine and of water vapour and is probably due to a photoactive bromine hydrate of composition $Br_2,H_2O$. This hydrate is strongly adsorbed by glass surfaces and the relationship between the concentration in the bulk and the surface phases can be expressed in the form of an adsorption iso-

therm. The hydrate may be displaced from glass surfaces by water. The Budde effect was not observed on illumination of moist bromine with light of wave-length longer than $\lambda = 5800$ Å.

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