THE PHOTOCHEMICAL DECOMPOSITION OF GASEOUS SULPHUR DIOXIDE.

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The most important generalisation in photochemistry is that first stated by von Grotthus, namely, that only those waves which are absorbed by a substance can be photochemically active.

No simple relation exists between the magnitude of the absorption and the chemical action produced. It is, however, fairly generally believed that when a substance shows chemical activity under the influence of light, then light of *any* wave-length which is absorbed by the substance (within the region of the band) will be effective in producing activity. The experimental evidence in this connection is however somewhat limited. One of the objects of the present investigation was to test the validity or otherwise of this view.

The reaction chosen was the photochemical decomposition of sulphur dioxide gas, which is known to form sulphur and oxygen, the latter being very largely used up to form sulphur trioxide.[2] The method adopted was to employ a source of radiation which would give a line spectrum extending generally over the same region as that occupied by the absorption band of sulphur dioxide, and then to proceed to cut out lines from the ultra-violet end of the spectrum until it was found that the substance was no longer decomposed. By comparing the results with the known absorption of the gas it should be possible to test the statement referred to.

The source of light was a Schott uviol mercury vapour lamp 40 cm. in length. The lines emitted by this lamp cover the region $700\mu\mu$ to $253\mu\mu$ which includes the first or "near" band of sulphur dioxide with its head at $291{\cdot}6\mu\mu$. The lamp was worked at a constant current of 2·4 amp., the p.d. across the terminals being 35 volts.

The sulphur dioxide gas, freed from sulphur trioxide and partially dried by passage over phosphorus pentoxide, was contained in a uviol tube (39·5 cm. in length, external diameter 4 cm., thickness of glass wall, 1 mm.), placed at a distance of 5 cm. from the lamp. The initial pressure of SO_2 was in all cases 600 mm. of mercury. The time of exposure varied from 4 to 8 hours. After exposure, caustic soda solution was run into the tube, the sulphate being determined analytically, the sulphur dioxide present initially being obtained from the pressure and temperature of the gas, this result being also checked by direct analysis. The quantity of free oxygen

[1] Communicated by Prof. W. C. McC. Lewis.

[2] *Cf.* Coehn, *Zeitsch. Elektrochem.*, **21**, 545, 1907.

was inappreciable as was to be expected in view of Coehn's observation and the relatively small value for the total decomposition obtained under the conditions employed.

After exposure a very slight deposit of solid was observed in the tube. This was shown to be sulphur in the following way. A series of ten successive experiments, each lasting 4 hours was carried out. After each exposure the vessel was simply evacuated and refilled with sulphur dioxide. Finally the vessel was evacuated and refilled with dry air three or four times and washed with water and alcohol to remove all trace of acid. Free sulphur was definitely shown to be present by the method of Gil.[1]

The actual primary photochemical process may either be a dissociation of the SO_2 molecule into atomic sulphur and molecular oxygen, or may simply consist in the activation of a sulphur dioxide molecule. In either case the final result is expressed by—

$$3SO_2 = 2SO_3 + S.$$

Experimental Results.

Coehn,[2] using a quartz mercury lamp on 6 to 9 amps. has shown that sulphur dioxide, enclosed in an annular space surrounding the lamp, is decomposed to the extent of 67 per cent., but when a uviol sheath is interposed, the decomposition is reduced to 14 per cent. This indicates that wave-lengths as long as $253\mu\mu$ are effective for the decomposition, but since the first absorption band of SO_2 extends to $318\mu\mu$ on the long wave side of the head, Coehn's result is far from showing that radiation of any wave-length within the band limits would be effective. For this reason measurements were carried out using the uviol lamp with a series of filters, the details of which are given later. The values for the decomposition of the gas under the influence of different qualities of light are given in the table below.

Temperature of Gas, 16-18° C. Initial Pressure, 600 mm.

Reference No. of Experiment.	Nature of Light, Filter and Time of Exposure.	Total Decomposition.
		Per cent.
1	Lamp alone, 8 hours	3·5
2	Lamp alone, 4 hours	3·4
3	Plate glass filter, 8 hours	0·0
4	One uviol sheath, 8 hours	3·4
5	Two uviol sheaths, 8 hours	3·4
6	Three uviol sheaths, 8 hours	3·2
7	White transparent glass, 8 hours	3·2
8	*p*-toluidine filter, 8 hours	3·3
9	*β*-naphthol filter, 8 hours	0·0
10	Lamp alone, acting on specially dried gas for 8 hours	2·8

(In the above table percentage decomposition represents grams per 100 grams of original SO_2.)

All the experiments, with the exception of No. 10, were carried out with gas which had been passed fairly rapidly over phosphorus pentoxide. A further increase in the water vapour content was found to be without effect upon the results. When the sulphur dioxide is specially dried, by

[1] *Zeitsch. anal. Chem.*, **33**, 54, 1894. [2] *Loc. cit.*

passing it slowly over P_2O_5, the decomposition value of the photostationary state dropped from 3·5 per cent. to 2·8 per cent.

Nature and Effectiveness of the Filters.

Experiments Nos. 1 *and* 2. *Vessel Wall without Additional Filter.*—It will be observed that practically the same amount of decomposition was obtained after 4 hours' exposure as after 8 hours. This indicates a photostationary state corresponding to the physical and dimensional conditions employed. This is attained in less than 8 hours. In all subsequent experiments an exposure of 8 hours was employed to obtain comparable results. Photographs were taken, on a Hilger quartz spectrograph, of the spectrum of the uviol lamp alone and also with one uviol sheath as filter. The line 253$\mu\mu$ is shown "strong" in the spectrum of the lamp alone, but "very weak" in that of the lamp with one sheath, whilst other lines are diminished in intensity.[1] It is to be remembered that it is under the latter condition that the present experiments have been carried out, as the gas itself is enclosed in a uviol sheath. The general trend of subsequent results strongly suggests that no line which is not found to be "moderately strong" can effect decomposition.

The results of experiments 1 and 2, when we take into account the corresponding spectrum photograph indicate that sulphur dioxide can be decomposed by radiation as long as 274$\mu\mu$. Although the uviol lamp emits wave-lengths as short as 253, 265, and 269$\mu\mu$, these barely get through a sheet of uviol glass, *i.e.* they cannot effectively penetrate the reaction vessel.

Experiment 3. *Vessel Wall + Plate Glass Filter.*—In this case no decomposition was observed. The plate glass transmitted no line of wave-length shorter than 334$\mu\mu$. This line is however transmitted moderately strongly. It follows that the decomposition must be brought about by one or more of the lines 313, 302, 297, 289, 280, and 274$\mu\mu$, known to be emitted by the lamp.

Experiment 4. *Vessel Wall + One Uviol Filter.*—The corresponding spectrum photograph was taken through two uviol sheaths in order to allow for the vessel wall, and similar procedure was adopted in the case of additional filters. The lines transmitted in this case are four in number, namely, 313, 302, 297, and 289$\mu\mu$. The observed decomposition amounted to 3·4 per cent.

Experiment 5. *Vessel Wall + Two Uviol Filters.*—Under these conditions the decomposition is identical with that of the previous case. The lines transmitted were found to be 313, 302, and 297$\mu\mu$.

Experiment 6. *Vessel Wall + Three Uviol Filters.*—A slightly lower decomposition value was obtained, namely, 3·2 per cent. The spectrum photograph is indistinguishable from that of the previous case. Obviously further use of uviol sheaths would be of little value.

Experiment 7. *Vessel Wall + White Transparent Glass.*—The spectrum photograph showed that this specimen of glass transmitted no light of wave-length shorter than 297$\mu\mu$ and the latter only feebly as compared with the effect of the uviol sheaths. The decomposition with this filter

[1] The terms "strong," "weak," etc., refer to an approximate system of estimating the relative intensities of the various lines in the subsidiary spectrographic measurements which were carried out in connection with the investigation of the photochemical change. Since the relative intensities have not been obtained in quantitative and numerical form, details of this portion of the work have been omitted.

amounted to 3·2 per cent. From this result it can be inferred that one or more of the wave-lengths 313, 302, and 297$\mu\mu$ are effective in bringing about the decomposition. From the relative intensities of the three lines it becomes very probable that the 313$\mu\mu$ line is mainly responsible for the decomposition. To test this a filter was sought for, which would leave the 313$\mu\mu$ line as the shortest line being transmitted into the reaction vessel, and which, at the same time, would not greatly diminish the intensity of this line. The filter referred to in the next case was found to fulfil this function.

Experiment 8. *Vessel Wall + Filter of p-Toluidine between two Uviol Sheaths.*—A solution of *p*-toluidine containing 0·107 gram in 20 c.c. alcohol was prepared according to Krüss.[1] Krüss states that this filter when used in a thickness of 0·8 mm. absorbs all light between 308$\mu\mu$ and 274$\mu\mu$. This was verified spectrographically. An experiment with this filter showed decomposition of sulphur dioxide to the extent 3·3 per cent. This demonstrates that the line 313$\mu\mu$ is capable of decomposing the sulphur dioxide, and further that this line alone accounts for more than 94 per cent. of the total decomposition effected by the uviol lamp. In contrast with this it may be recalled that the next longer line in the uviol spectrum, namely 334$\mu\mu$, causes no decomposition at all (*cf.* expt. 3).

Garrett[2] has shown that sulphur dioxide gas has a first absorption band commencing at 318·2$\mu\mu$ with its head at 296·1$\mu\mu$ and a second band commencing at 232·4$\mu\mu$ approximately and continuing beyond the limit of the ordinary plate (210$\mu\mu$). Thus the line 313$\mu\mu$ lies just within the first absorption band and on the longer wave-length side of the band head. The above observations tend therefore to confirm the view that any wave-length within the limits of a band can activate or decompose the substance.

Experiment 9. *Vessel Wall + β-Naphthol Filter within Two Uviol Sheaths.*—The fact that the lines in the region 302$\mu\mu$ to 274$\mu\mu$ have no appreciable effect is probably due to their weak intensity. Thus in Cohen's work, when the 253$\mu\mu$ was present as a strong line, it was very efficacious, but in the present work, where it is reduced to a weak line, it appears to have practically no effect. The argument that very weak lines have no appreciable influence photochemically was confirmed by the use of a β-naphthol filter. An alcoholic solution of β-naphthol (containing 0·144 gram in 50 c.c. alcohol),[3] when used as a filter, absorbs the 313$\mu\mu$ line to some extent and transmits it as a weak line. It also transmits the 302 and 297$\mu\mu$ as weak lines. Using this filter no decomposition at all is observed.

The Thermal Decomposition of Sulphur Dioxide.

In applying quantum considerations to the energetics of a chemical process (occurring under thermal conditions), it is necessary to calculate in terms of the head of the band which is responsible for the decomposition or activation of the given molecular species. The results obtained in the photochemical experiments described above indicate that in the case of SO_2 the band involved is that having its head at 296·1$\mu\mu$, and consequently the critical increment E_{SO_2} of this substance reckoned per gram-molecule is 96,700 cals.

[1] *Zeitsch. Physikal. Chem.*, **51**, 257, 1905.
[2] *Phil. Mag.* [vi.], **31**, 505, 1916.
[3] *Cf.* Krüss, *loc. cit.*

On the quantum theory of thermal chemical change, the heat of reaction is related (exactly, in the case of unimolecular processes, approximately, in the other cases) to the critical increments of reactants and resultants thus—

heat evolved = (critical increment of resultants) − (critical increment of reactants).

This expression has already been applied by W. C. M. Lewis[1] to the case of the thermal formation and decomposition of sulphur dioxide. The heat evolved in the formation of one gram-molecule of SO_2 from the *gaseous* components, sulphur and oxygen, is 82,000 cals. The critical increment of one gram-atom of gaseous sulphur and one gram-molecule of oxygen was calculated to be of the order 103,000 cals., whence the critical increment of the SO_2 molecule is 185,000 cals. per gram-molecule, which corresponds to a wave-length $153\mu\mu$. We have seen, however, that SO_2 can be decomposed by a much longer wave-length ($296{\cdot}1\mu\mu$) so that the critical increment calculated in the above manner is apparently far too great. In this calculation it was assumed that *atomic* sulphur was actually produced by the dissociation of SO_2 and that consequently for the formation of SO_2 it was necessary to use the data representing the absorption of energy necessary to produce one gram-atom of sulphur from the S_8 molecules which chiefly compose the vapour of sulphur over the region 200° to 500°. This energy term is itself of the order of 50,000 to 70,000 cals. and it is evident that the excessive value obtained in the previous calculation for the critical increment of SO_2 is due in the main to the introduction of this quantity.[2]

In view of the photochemical decomposition occurring at a wave-length as long as $296{\cdot}1\mu\mu$ it seems necessary to assume that in the formation of SO_2 from *gaseous* sulphur and oxygen the atom of sulphur is not involved, but that instead we have to do with the simplest molecular form S_2. This indicates that in the photochemical process we are dealing with the activation of a SO_2 molecule rendering it capable of reacting with a second molecule rather than with a direct dissociation of an individual SO_2 molecule.

The gaseous S_2 molecule has a critical increment in the sense that over the temperature range mentioned the vapour consists of S_8 molecules. From the data available Lewis has calculated that the energy 21,500 cals. approximately must be absorbed for the production of one gram-molecule of S_2 from S_8. Further the oxygen molecule is known to possess two absorption bands in the short infra-red region, *viz.* at $3{\cdot}2\mu$ and $4{\cdot}8\mu$,[3] of which the latter is the more marked. The critical increment corresponding to a wave-length $4{\cdot}8\mu$ is 6000 cals. in round numbers, per gram-molecule.

It is not clear whether one or both of the oxygen molecules has to be activated in order to react with S_2—since the stoichiometric equation, $S_2 + 2O_2 = 2SO_2$, probably includes two bimolecular processes. We can only say therefore that the energy required for the partial activation of the

[1] *Trans. Chem. Soc.*, **115**, 182, 1919.

[2] It may be pointed out perhaps that the calculation of Lewis is correct in principle for the dissociation of SO_2 into atomic sulphur and molecular oxygen. A revision of the numerical values employed would lead to a value somewhat lower than 185,000 cals., but still much greater than the value inferred from the photochemical result.) A wave-length corresponding to the "second" or "further" absorption band of SO_2 would be likely to decompose SO_2 into atomic sulphur and oxygen, but the photochemical result appears to indicate that the actual mechanism is one which follows a path of lower increments, for reactants as well as for resultants.

[3] *Cf.* Coblentz, *Carnegie Inst. Washington Pub.*, No. 35, 1905.

oxygen molecules lies between 6000 cals. and 12,000 cals. Adding this to the increment for S_2, namely 21,500 cals., it follows that the total increment for $(S_2 + 2O_2)$ lies between 27,500 and 33,500 cals. Applying the heat-quantum relation to the stoichiometric equation given above we obtain :—

$$2 \times 82{,}000 = 2E_{SO_2} - \begin{Bmatrix} 27{,}500 \\ \text{or} \\ 33{,}500 \end{Bmatrix}.$$

Whence, $2E_{SO_2}$ lies between 197,500 and 191,500
or E_{SO_2} lies between 98,700 and 95,700 cals.

a value which agrees satisfactorily with the critical increment, 96,700 cals., calculated from the photochemical decomposition. A good deal of arbitrariness, however, surrounds the choice of the value for the critical increment of (low, partial) activation of the oxygen molecule. Taking the value 96,700 cals., obtained from the photochemical conditions, as correct, it would follow that the sum of the critical increments of gaseous $(S_2 + 2O_2)$ is 29,500 cals. This relatively low value, together with the great evolution of heat accompanying the union of sulphur and oxygen, indicates that sulphur and oxygen should react easily and that the sulphur dioxide molecule should be thermally very stable ; the latter conclusion is in agreement with the conclusions of von Wartenberg.[1]

Summary.

1. The decomposition of sulphur dioxide gas under the action of light radiated from a uviol mercury vapour lamp has been investigated, and the resulting photostationary state, characteristic of a given set of conditions, determined, using a number of different light filters.

2. It is shown that the wave-length chiefly responsible for such decomposition of the gas is $313\mu\mu$. It is noteworthy that the shorter wave-lengths, also present in the above source of radiation, contribute very little to the decomposition. The wave-length $313\mu\mu$ lies within the first absorption band of sulphur dioxide (at a pressure of 600 mm.), but does not correspond with the head of the band, already known to occur at $296{\cdot}1\mu\mu$. The actual wave-length producing maximum decomposition depends on the nature of the source of radiation, *i.e.*, upon the intensity distribution of the emission spectrum.

3. Of the radiation emitted from the uviol lamp the longest wave-length capable of decomposing sulphur dioxide is the $313\mu\mu$ line itself. The conclusion is drawn that any wave-length within the absorption band of the substance is capable of bringing about decomposition provided the intensity is sufficiently great.

4. The bearing of the photochemical decomposition of sulphur dioxide upon the critical increment of the *thermal* union of oxygen and sulphur vapour is discussed. It is concluded that the molecule S_2 as distinct from the atom is involved in this process.

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[1] *Zeitsch. anorg. Chem.*, **56**, 320, 1908.