CCLXI.—*The Photochemical Decomposition of Chlorine Monoxide.*

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IT is well known that the mechanisms of most photochemical changes are very obscure, and that this is due to the primary reactions between the absorbing substances and the light being obscured by a complex series of subsequent reactions, during which the energy absorbed and liberated in the reaction is redistributed in an unknown manner among other molecules. As radiant energy is only absorbed in quanta, those photochemical reactions in which the subsequent reactions are not extensive will provide a ratio Molecules reacting/Quanta absorbed not far removed from unity. The rarity of such reactions is probably exaggerated, because the most striking photochemical reactions are those of high so-called "light sensitivity."

In continuation of previous work (this vol., p. 1199) the photochemical decomposition of gaseous chlorine monoxide in blue and violet light has been investigated. The source of light was a 1000 c.p. "Pointolite" lamp. A condensed beam of light, filtered through solutions of copper sulphate and of crystal-violet, passed directly into the photochemical cell. The energy in the radiation was determined in three ways, which gave concordant results; first, as previously described (*loc. cit.*); secondly, by calibrating a Melloni thermopile with a small, thin, flat coil in which known amounts of electrical energy were expended, the coil being placed as close as possible between the face of the thermopile and a blackened metal plate; and, thirdly, by the use of a special air-thermometer. This consisted of a cylindrical glass vessel with a plane side through which the light entered, to fall on a screen inside made of the thinnest rice paper blackened with Indian ink. A coil of constantan wire wound on the paper served for calibrating, and pressure changes due to the heating effect of the radiation were measured on an aniline–water differential manometer. Although the thermopile and potentiometer is a more sensitive arrangement, it is thought that this air-thermometer is more accurate for absolute measurement, because the heating by the radiation and by the calibrating current take place under closely similar conditions.

The absorption measurements were made with the thermopile and potentiometer. The photochemical cell consisted of a piece of glass tubing 3·2 cm. in diameter and 4·5 cm. long, the ends of which were closed by pieces of thin plate glass fused on, and fitted with two capillary tubes and taps. It was filled by condensing in it a quantity of liquid chlorine monoxide, prepared by passing dry chlorine through a long tube containing precipitated mercuric oxide which had previously been heated for several hours at 350°, and allowing the liquid to evaporate. The photochemical reaction was followed by measuring the changes of pressure on exposure, the cell being connected by a ground glass joint through a capillary " air buffer " to a sulphuric acid manometer. The vessel was immersed in water at constant temperature before initial and final pressures were read.

Several filters isolating the blue and violet rays were used. In the calculation of the number of quanta absorbed a mean wavelength of 4600 Å.U. has been employed; that is, $h\nu = 4{\cdot}28 \times 10^{-12}$ erg.

Summary of Results.

Quanta per second in light $\times 10^{-16}$.	Absorption.	Molecules decomposed per second $\times 10^{-16}$.	$\frac{\text{Molecules decomposed}}{\text{Quanta absorbed}}$.
15·4	0·59	21·0	2·30
15·2	0·52	17·3	2·19
14·4	0·58	17·4	2·09
12·0	0·36	9·92	2·30
11·7	0·49	12·7	2·22
11·3	0·46	11·6	2·22
10·2	0·42	10·8	2·52
8·19	0·25	4·45	2·18
7·82	0·28	4·66	2·13
6·86	0·54	9·25	2·50
5·38	0·60	7·1	2·20

The amount of decomposition in the above experiments was of the order of 3 per cent.

More accurate comparative experiments on the same sample of gas showed that the photochemical rate was strictly proportional to the light intensity over a range of 1 : 4, a rotating sector being used to vary the light intensity.

The chlorine monoxide contained varying quantities of chlorine as an impurity, the elimination of which apparently is not easy. The uniformity of the results suggests, however, that the presence of chlorine does not seriously affect the rate of decomposition.

The results indicate that two molecules are decomposed for each quantum absorbed; the reaction therefore seems a comparatively simple one. Two alternative and indistinguishable mechanisms explain the results.

Either the decomposition is unimolecular,

$$Cl_2O + h\nu \longrightarrow \text{“active”}\ Cl_2O \longrightarrow Cl_2 + O,$$

this being the only possible unimolecular decomposition in violet light (see previous reference), and is followed by a spontaneous reaction,

$$Cl_2O + O \longrightarrow Cl_2 + O_2 + 91{,}000 \text{ cal.},$$

or the change is

$$Cl_2O + h\nu \longrightarrow \text{“ active ” } Cl_2O,$$

followed by

$$\text{“ active ” } Cl_2O + Cl_2O \longrightarrow 2Cl_2 + O_2 + 95{,}000 \text{ cal.}$$

Both possibilities satisfy the condition that the spontaneous reactions shall be exothermic. It should be noted that the very large heat evolutions in either case do not lead to further decomposition, as would be expected if the views of Baly (*Trans. Faraday Soc.*, 1922, **17**, 588), that this energy would be liberated at infra-red frequencies capable of re-absorption, are correct.

When chlorine *peroxide* is exposed to light a more complex decomposition takes place, with formation of large quantities of an unstable brown liquid. This disappears with formation of white fumes when a trace of water vapour is admitted. Traces of white fumes are also observed when chlorine monoxide which has been exposed to light is allowed to come into contact with moist air. It seems that in both cases some formation of other oxides of chlorine occurs besides the simple decomposition. These reactions are being further investigated.

Summary.

Two molecules of chlorine monoxide in the gaseous state appear to be photochemically decomposed for each quantum of blue and violet light absorbed. The mechanism of the reaction has been discussed on this basis.

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