[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE ACTION OF LIGHT ON CHLORINE

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I. Introduction

A comparison of the photochemical literature on the reactions and other properties of illuminated chlorine on one side and of the results of a more physical investigation of its absorption spectrum on the other, indicates that, at present, a certain controversy exists between two main opinions on the nature of the primary action of light on chlorine.

Several studies of the absorption spectra of the halogens, of the more recent ones particularly that of Kuhn,[2] demonstrated the existence of series of absorption bands converging on the short-wave side to a limit, from which a continuous absorption extends toward the ultraviolet. On the basis of these observations Franck[3] suggested that chlorine and other halogen molecules are dissociated into atoms—a normal and an excited atom—on absorption of radiation frequencies belonging to the continuous absorption region and that absorption in the region of the band spectrum causes formation of activated molecules, capable in general of reëmission of absorbed light energy as fluorescence radiation. Franck's conclusions were later confirmed by Dymond[4] who showed that fluorescence is emitted by iodine molecules only on absorption of light of longer wave length than 5000 Å.—the convergence limit of this halogen. It may be pointed out that, according to physical researches, a further condition for the realization of fluorescence in halogen vapors is their low pressure. Thus, Wood and Speace[5] found that excited iodine molecules can be deactivated on collisions not only in presence of foreign gases but also in pure iodine vapor.

A number of different theories on the nature of the primary action of light on chlorine have been advanced recently by several photochemists, their common experimental basis being the observation of Coehn and Jung[6] that a pure and dry mixture of chlorine and hydrogen does not react on illumination by visible and near ultraviolet light. The theory of Norrish,[7] however, who located the chemical action of light on chlorine in the water-chlorine film on the walls of the containing vessel, has been recently disproved by decisive experiments of Coehn and Heymer.[8] Fur-

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[2] Kuhn, *Z. Physik*, **39**, 77 (1926).

[3] Franck, *Trans. Faraday Soc.*, **21**, 536 (1925).

[4] Dymond, *Z. Physik*, **34**, 553 (1925).

[5] Wood and Speace, *Physik. Z.*, **15**, 317 (1914).

[6] Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1924).

[7] Norrish, *J. Chem. Soc.*, **127**, 2317 (1925).

[8] Coehn and Heymer, *Ber.*, **59B**, 1794 (1926).

ther, primary formation of activated chlorine molecules[9] or of chlorine atoms[6] has been occasionally suggested, the catalytic action of water being attributed to secondary processes. These theories coincide, at least in broad terms, with the deductions from the study of the absorption spectrum of chlorine, since, as Franck[3] pointed out, dissociation into atoms must be preceded by activation of chlorine molecules. Only further investigations can decide to which of these stages the photochemical reactivity of chlorine should be attributed. A distinctly different theory has been advanced by Weigert,[10,11] who suggested that water molecules are necessary for the accomplishment of the *primary* photochemical process in chlorine. If this latter is absolutely pure, all absorbed light energy is reëmitted by chlorine molecules as isochromatic fluorescence and only in presence of water or certain other molecules can the absorbed radiation be converted into chemical energy or into heat. The special nature of this action of foreign molecules was also discussed by Weigert and he suggested for instance that, in the hydrogen-chlorine reaction, water acts through its di-pole nature, facilitating an inner photo-electric effect between hydrogen and chlorine. As an important support of his theory Weigert cited the results of investigations on the Budde effect—the expansion of chlorine gas on illumination. Since Budde's[12] discovery, more recent investigations have demonstrated that the effect is due entirely to the conversion of absorbed light energy in chlorine into heat.[13,14] Further, it was found that *dry* chlorine shows a very small Budde effect and that the effect can be increased considerably by admission of some moisture to the gas.[15] Ludlam[16] arrived at a similar conclusion, experimenting with bromine.

In the opinion of Weigert this observed absence of the heating of dry chlorine is a direct evidence that the absorbed light energy can be converted into heat only in presence of moisture and is reëmitted as fluorescence by pure gas. Lewis and Rideal[17] went even further. On investigating the Budde effect in bromine vapor, they suggested that only a definite molecular compound Br_2-H_2O is photosensitive and that all light absorbed by simple bromine molecules is re-radiated again as fluorescence.

Summarizing, it may be pointed out that all theories which assume the presence of foreign molecules to be necessary for the primary photo-

[9] Chapman, *Trans. Faraday Soc.*, 21, 547 (1925).

[10] Weigert, *Z. physik. Chem.*, **106**, 426 (1923).

[11] Compare also Cathala, *Compt. rend.*, **181**, 33 (1925).

[12] Budde, *J. prakt. Chem.*, **7**, 376 (1873).

[13] Richardson, *Phil. Mag.*, [5] **32**, 221 (1891).

[14] Bevan, *Trans. Roy. Soc.* (*London*), **202**, 90 (1904).

[15] Shenstone, *J. Chem. Soc.*, **71**, 471 (1897).

[16] Ludlam, *Proc. Roy. Soc. Edinburgh*, **34**, 197 (1924).

[17] Lewis and Rideal, *J. Chem. Soc.*, **128**, 583 (1926).

chemical process assume at the same time that pure chlorine (and similarly bromine) does fluoresce. With the test of this latter conclusion we are concerned in the experiments now to be described.

II. Experimental Arrangement

In order to obtain gas of a known photochemical inactivity the method of Coehn and Jung[6] of purification and drying of chlorine was closely followed. The apparatus consisted of a distilling arrangement for chlorine, of a quartz spiral manometer (quartz-Pyrex graded seal being used) and of two cylindrical vessels 23 × 3.5 cm. with sealed-on, optically clear Pyrex glass plates. These latter were necessary since, in search of chlorine fluorescence, all light from the illuminating source scattered on glass surfaces should be avoided as far as possible. The process of sealing-on proved to be not very difficult and although the edges of the plates were slightly damaged, their middle areas of about 2 cm. diameter remained entirely intact. Each vessel had two side tubes, one of which contained an inner glass seal separating a small volume (about 0.75 cc.) filled with water vapor at atmospheric pressure, the other being used for freezing out chlorine in some of the experiments. Stopcocks in the part of the apparatus behind the high-vacuum pump were entirely avoided; instead, inner glass seals operated by iron cores (enclosed in glass) and constriction for sealing-off were used. The whole apparatus, including the manometer, was baked out in a vacuum[18] on two successive days, the test for tightness being that the pressure in the McLeod gauge did not increase overnight to more than 10^{-5} mm. The mercury-vapor trap was cooled by liquid air only during the second baking out and subsequent operations.

Chlorine from a half-empty chlorine tank was three times distilled in a vacuum at —112° (the temperature of melting carbon disulfide). Each time only about three-fourths of the chlorine was distilled over, the rest being sealed off. Finally, chlorine was condensed in the side tubes of the cylindrical vessels and these were sealed off from the rest of the apparatus. Of three attempted fillings only two could be carried out successfully. The first time chlorine of about 500 mm. pressure was prepared and preliminary measurements were taken. These results, although less exact, confirm entirely the final experiments with the third filling and chlorine of about 2 atmospheres' pressure.

III. Absorption of Light in Moist and Dry Chlorine

It may be concluded from Kuhn's[2] description of his experimental arrangement that he worked with fairly dry chlorine. It appeared to be of interest, nevertheless, to measure the wave length of the bands' convergence limit in the available chlorine of highest purity. For photographs of the chlorine absorption spectrum a Hilger glass spectograph, with a large direct vision prism inserted to increase the dispersion, was employed.[19] Since the chlorine layer used was only 23 cm. long, the light absorption in the green was very weak even at 2 atmospheres' pressure. Therefore, the measurement of single bands with subsequent calculation of the convergence limit had to be abandoned. Still, study of the plates with a micrometer, as also curves made on the densitometer, permitted

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[18] For details compare Dushman, High Vacuum Technique, *Gen. Elec. Rev.*, Schenectady, **1922**.

[19] The author is indebted to Professor A. Shenstone of the Department of Physics for his kind advice and help during this part of the work.

an approximate determination of the convergence limit at 4790 Å. The reference spectrum used was that of an iron arc. The accuracy of this determination is about 10 Å. (1 mm. on the plates), so that the result obtained is to be considered identical with Kuhn's more exact value 4785 Å. Determinations of absorption coefficients of chlorine in monochromatic light of different wave lengths were carried out with unusual precision by Halban and Siedentopf.[20] They studied also the influence of moisture and found in light of three different wave lengths no appreciable difference between moist and fairly dry chlorine. A question which is not decided by these experiments and which is of importance for the following discussion is whether the total absorption in polychromatic light is markedly different in very dry and in moist chlorine. For the following measurements the glass vessels containing chlorine were placed in a blackened box with two openings rigidly adjusted on an optical bench. As light source a 100-watt Pointolite lamp was used, which in order to increase the intensity of shorter wave lengths was overloaded and burned on 1400 m. amps. and 115 volts. A system of lenses and diaphragms isolated a parallel beam of light, the square section of which was about 2.5 sq. cm. Immediately behind the chlorine vessel was placed a Moll thermopile of surface (3.14 sq. cm.) larger than the area of the light beam. The only light filter used for these and later experiments was a concentrated solution of ferrous sulfate (and a small quantity of hydrazine sulfate) which absorbed infra-red and a part of the extreme red radiation. Table I gives the results of measurements with chlorine of two atmospheres' pressure.

TABLE I

LIGHT ABSORPTION IN CHLORINE; PER CENT. OF THE TOTAL RADIATION

Dry chlorine	8.45;	9.95;	8.22;	8.40;	av. 8.75
Moist chlorine	9.89;	7.91;			av. 8.90

Each of these values is an average of about 20 single readings, half of them with the vessel filled with chlorine, half with the empty vessel, chlorine being frozen out by liquid air. The deviations of the values given are rather large—10% and more from the final averages. They are due not to the inexactness of the thermopile readings, but to the impossibility of keeping the light intensity constant to more than 1–2% during the longer time intervals necessary for freezing out and warming up of chlorine and eventually of water, this being admitted to the chlorine by breaking the inner glass seals mentioned earlier.

IV. Fluorescence of Dry Chlorine

The optical arrangement described in the former section was used also for the study of chlorine fluorescence. This part of the work included

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[20] Halban and Siedentopf, *Z. physik. Chem.*, **103**, 71 (1923).

experiments with the thermopile and spectrophotographic tests. The determination of the light absorption in chlorine was carried out with the sensitivity of the thermopile–galvanometer system reduced to 7.15% by series and shunt resistances. In order to test this calculated ratio of sensitivities, the light intensity of a special standard lamp was measured with full and reduced sensitivity. The ratio of scale deflections so determined was practically identical with the calculated, 0.073. The thermopile with full sensitivity of the circuit was placed at a distance of 1 cm. from the side wall of the chlorine vessel at a right angle to the light beam. Assuming a uniform distribution of fluorescence over the hypothetical radiating surface (of which the thermopile is a part) (399 sq. cm.), 0.0082 of the total emitted radiation should fall on the light sensitive surface of the thermopile. This calculation is somewhat unfavorable, since the thermopile was put close to that end of the vessel where the light beam entered and a greater part of the fluorescence should be concentrated here on account of the greater light absorption in the initial layers of chlorine. Further, in front of the thermopile was a polished metallic cone of 1 cm. length and 4 sq. cm. open front surface. If all light falling on the side walls of the cone was reflected to the light-sensitive surface of the thermopile, then the above fraction should be increased to about 0.013. The scale deflection corresponding to the light energy absorbed by chlorine was on the average 16.1 mm. (with reduced sensitivity). Thus, if all the light absorbed is reëmitted by dry chlorine as fluorescence, a deflection of at least 1.85 mm. should be expected. Measurements with the vessel filled with chlorine and with the empty vessel yielded 0.43 and 0.31 mm., respectively, as averages of about 20 single readings for each value. The single readings fluctuated between —0.1 and +0.7 mm.

There were good grounds for believing that even these small deflections—their difference ("the fluorescence") does not amount to more than 5% of the calculated value—are due to some heating effects on illumination rather than to emission of visible light, since, on visual observation, the chlorine vessel remained entirely dark when the light beam was passed through it.

The Hilger spectrograph, without the additional prism and with the slit wide open, was adjusted in the box at right angles to the light beam and at 2 cm. distance from the side walls of the chlorine vessel. Photographs taken with exposures of from one to six hours and with the vessel filled with chlorine or empty showed in no case even the slightest trace of spectrum image. On the other hand, when the spectrograph was placed behind the chlorine vessel in the path of the light beam, with a ground glass plate in front of the slit at a distance of 2 cm., a well-developable image of the spectrum was obtained even after an exposure of one **second.**

From these data it is easily calculable that the fraction of absorbed light energy which is reëmitted as fluorescence by dry chlorine must be considerably smaller than the upper limit of 5% determined by means of the thermopile.

V. Discussion

The results of the experiments described are these: the structure of the absorption spectrum and the total absorption of chlorine are not appreciably changed by extreme drying; only an extraordinarily small fraction of the absorbed light energy can be reëmitted as fluorescence even in very dry chlorine. On the other hand, there is little doubt as to the reality of the decrease of the Budde effect on drying chlorine. These observations of different investigators seem to contradict each other. Evidently, since fluorescence is absent and the extent of absorption is unchanged, it must be concluded that one and the same amount of light energy introduced may or may not cause a heating effect, depending only on the presence or absence of impurities in chlorine.

It is rather difficult to reconcile the new data with the theories of Weigert and others who assume that, for the primary photochemical process in chlorine, the presence of foreign molecules is necessary. The absence of fluorescence and their denial of the dissociation of "free" chlorine molecules leave no choice but the conclusion that the absorbed light energy is converted by these "free" molecules into heat, and this is in strict disagreement with the observations on the Budde effect. An assumption that the absorbed light energy is somehow stored up (in absence of water) in activated chlorine molecules, an assumption rather improbable in itself, is further decidedly disproved by experiments of Bodenstein and Taylor[21] and of Marshall[22] on the life of activated chlorine.

The difficulty in reconciling the existing data is not entirely removed by accepting the theory that the primary photochemical process in chlorine is, independently of the presence of impurities, a dissociation into atoms. Since under these circumstances the process which contributes to the warming up of the illuminated gas would be almost entirely the recombination of chlorine atoms to molecules, it must be assumed that, in absence of water molecules, this process is very slow in the gas phase and takes place almost exclusively on the dry walls of the containing vessel. Thus, the absorbed light energy will be transported to the walls and cannot cause the Budde effect on account of the large heat capacity and relatively good heat conductance of the glass walls. The experiments described give, of course, no indication as to the nature of the catalytic action of water on the rate of recombination of chlorine atoms.

A certain difficulty with the explanation of the Budde effect here ad-

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[21] Bodenstein and Taylor, *Z. Elektrochem.*, **22**, 202 (1916).

[22] Marshall, *J. Phys. Chem.*, **30**, 757 (1926).

vanced arises from the thermodynamic consideration that in such a case the rate of thermal dissociation of chlorine molecules should also be accelerated by water vapor.

Summary

1. A brief account of theories on the nature of the primary photochemical process in chlorine has been given.

2. Earlier measurements and the data now obtained show that extreme drying of chlorine does not change appreciably either the structure of its absorption spectrum or the total amount of light energy absorbed.

3. Measurements of a possible fluorescence in dry chlorine reveal that certainly less than 5% of the absorbed light energy is reëmitted as fluorescence.

4. It has been suggested, in order to reconcile these experimental results with the known influence of moisture on the Budde effect, that chlorine (or other halogen) is dissociated into atoms on absorption of light energy in the region of continuous absorption independently of its degree of purity; water is assumed to have a catalytic influence on the rate of recombination of the atoms and, therefore, also on the rate of thermal dissociation of chlorine molecules.

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HEATS OF ADSORPTION ON POISONED AND HEAT-TREATED CATALYSTS

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In the preceding five years the non-uniform character of the catalyst surface has been developed by quantitative studies of adsorption, reaction kinetics, poisoning and promoter action on a variety of catalysts. This differentiation in the catalytic activities of the units in the catalyst surface has permitted an experimental attack on the problem of activation at the catalyst surface, a most important step in placing the study of contact catalysis on a scientific basis and in freeing catalysis from the bane of empiricism.

Experiments by Gauger[2] and by Wolfenden[3] on the ionization potentials of adsorbed hydrogen on hydrogenation catalysts have indicated that the hydrogen adsorbed on the more active portions of a catalyst surface may be atomic. These experiments were extended by Kistiakowsky[4]

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[2] Gauger, This Journal, **46,** 674 (1924).

[3] Wolfenden, *Proc. Roy. Soc.* (London), **110A,** 404 (1926).

[4] Kistiakowsky, *J. Phys. Chem.*, **30,** 1356 (1926).