CXXXVII.—The Photochemistry of Unstable Substances.

By Edmund John Bowen.

AMONG the various attempts to apply the quantum theory to the problems of chemical reactivity is the so-called law of the photochemical equivalence, first obtained by Einstein (Ann. Physik, 1912, **37**, 832), which is generally accepted as forming a basis for the consideration of photochemical reactions. The number of molecules reacting is equated to the number of quanta in the light absorbed by the system. This law was shown by Einstein to be the necessary average (and approximate) result from the radiation laws in the case of a photochemical "stationary state" having properties of a rather hypothetical character. The view now taken is to regard the law as founded on the quantum absorption of radiant energy, and therefore as equally applicable to "irreversible" photochemical reactions.

In the case of actual photochemical reactions, the ratio quanta absorbed/molecules reacting assumes various values from ∞ to about 10⁻¹⁰ (compare Bodenstein, Z. physikal. Chem., 1913, 85, 329). Important investigations of the experimental validity of the law have been made by Warburg (summary, Z. Elektrochem., 1920, 26, 54), Henri and Würmser (J. Phys. Radium, 1913, [v], 3, 305; Compt. rend., 1913, 156, 1012), and by Noddack (Z. Elektrochem., 1921, 27, 359). It appears that the law is closely followed in the reactions

 $\begin{array}{ccc} \text{HBr} & \longrightarrow & \text{H} + \text{Br} \\ \text{HI} & \longrightarrow & \text{H} + \text{I} \end{array} \right\} \text{ (Warburg) in ultra-violet light,}$

$$Cl_2 + 2CCl_3Br \longrightarrow 2CCl_4 + Br_2$$
 (Noddack) in violet light,

and in the reactions

and
$$\begin{array}{ccc} 3O_2 \longrightarrow 2O_3\\ 2O_3 \longrightarrow 3O_2 \end{array}$$
 (Warburg) in ultra-violet light,

if readily acceptable assumptions are made as to a primary photochemical process followed by spontaneous secondary thermal reactions.

Deviations from unity of the measured ratio quanta absorbed/ molecules reacting in other reactions are explained by Warburg and Nernst as due to three main causes :

(1) The quantum absorbed may not be large enough to bring about the primary change.

(2) The molecule may absorb a quantum, but may lose it again

by collision, the energy being degraded as heat ("deactivation by collision").

(3) Secondary spontaneous thermal reactions. Such reactions may form a chain, accounting for extraordinarily small values of the ratio (Nernst, Z. Elektrochem., 1918, 24, 335).

The first two causes make the ratio larger than unity; the third usually makes it smaller. So all actual cases are provided for.

In this investigation was studied the application of the law to the photochemical decomposition in violet light of carbon tetrachloride solutions of chlorine peroxide, chlorine monoxide, and nitrogen trichloride.

EXPERIMENTAL.

Materials.—The pure carbon tetrachloride of commerce was allowed to stand with chlorine peroxide, washed, dried with phosphoric oxide, and fractionally distilled.

Source of Light.—In order to reduce the necessary time of exposure of unstable solutions, an intense source of light is required. A carbon arc, taking 11 amperes at about 45 volts, with vertical, electromagnetically regulated negative electrode was used. The hand-fed positive electrode was horizontal, and was only 7 mm. in diameter to minimise wandering of the "spot." A permanent magnet deflected the arc so that the positive spot was situated at the extreme end of the electrode. With a condensing lens the light was concentrated on an aperture of area about 4 sq. cm., behind which the photochemical cell was placed. The blue and violet rays were isolated by means of trough filters containing solutions of ferrous ammonium sulphate and copper sulphate, and of crystalviolet.

The chief source of inaccuracy in the experiments was due to the fluctuations in the light intensity of the arc; this especially affected the absorption measurements. The inaccuracy on this account may reach 25 per cent.

Photochemical Cell.—A flat-walled cell was constructed, of internal width about 5 mm. and volume about 4.5 c.c., somewhat resembling a pyknometer in shape, and fitted with two taps lubricated with phosphoric acid. Filling was accomplished by forcing the solution through a capillary tip inserted through the bore of one of the taps. With this cell an accurately reproducible volume is employed at each filling, and the whole of the liquid can be removed for titration; auxiliary pipettes, involving exposure to air and loss of solute under the partial vacuum, are avoided; and loss of liquid during exposure is negligible.

Measurement of Energy.—The energy in the radiation employed was measured with a rough bolometer. A wide-angled cone of

about 20 ohms resistance, 2.5 cm. in diameter, was wound from 42-gauge silk-covered copper wire one layer thick, held together with a little shellac and blackened on the inside. The resistance change of this cone when heated by the radiation was measured against an approximately equal resistance composed of heavy-gauge manganin wire. It was calibrated by measuring its change of resistance when different amounts of electrical energy were expended in it. Three or four minutes were necessary for the instrument to come into equilibrium with the radiation.

For the measurement of the energy absorbed in the various experiments a Melloni thermopile of 56 antimony-bismuth pairs was found convenient. Readings were made on a potentiometer wire connected in series with a suitable high resistance and an accumulator; the arrangement being calibrated by comparison with the bolometer.

The wave-lengths absorbed in these experiments reached from about 4100 Å. to 4700 Å. In calculating the number of quanta, a representative mean wave-length 4450 Å. has been employed; that is, $h\nu = 4.42 \times 10^{-12}$ erg.

Chlorine Peroxide Solutions.

Chlorine peroxide, prepared in an all-glass apparatus by warming at 60° a mixture of 8 grams of potassium chlorate, 30 grams of crystallised oxalic acid, and 4 c.c. of water (Bray, Z. physikal. Chem., 1906, 54, 463, 569, 731), was passed into carbon tetrachloride. The gas and the solutions were dried with phosphoric oxide. The solutions are bright yellow and show a characteristic absorption spectrum consisting of bands in the blue and the violet equally spaced on a frequency scale, with maxima at 4675, 4520, 4370, and 4220 Å. approximately. The bands are much fainter in the longer wave region. This spectrum resembles that found by Käbitz (Diss., Bonn, 1905) for the gas. The solutions decompose slowly in the dark, the rate of decomposition depending on the free space in the vessel above the liquid.

In light, the decomposition may be represented stoicheiometrically

$$2\text{ClO}_2 \longrightarrow \text{Cl}_2 + 2\text{O}_2$$
,

the oxygen largely remaining in the solution in a supersaturated condition.

Chlorine peroxide and chlorine in presence of one another were estimated by addition to excess of potassium iodide and titration with sodium thiosulphate, first with the solution neutral, and then acidified with dilute acid (Bray, *loc. cit.*).

The reactions are :

Neutral sol. $3ClO_2 + 5I' \longrightarrow 2IO_3' + 3Cl' + 3I.$ Acid sol. $ClO_2 + 5I' + 4H' \longrightarrow Cl' + 2H_2O + 5I.$

Chlorine reacts equally in neutral and acid solutions :

 $Cl_2 + 2I' \rightarrow 2Cl' + 2I.$

Summary of Results.—

	Molecules	Quanta		
Conc. of ClO ₂	decomposed	per sec.	\mathbf{Mean}	
in gram-mol.	per sec.	in radiation	absorp-	Quanta absorbed
per litre.	$ imes 10^{-16}$.	imes 10–16.	tion.	Molecules decomposed
0.317	5.8	8.7	0.9	1.35
0.166	6.0	8.7	0.82	1.19
0.160	6.2	8.7	0.80	1.12
0.0945	5.03	8.7	0.74	1.28
0.0885	3.14	6.0	0.71	1.35
0.0856	4.75	8.7	0.70	1.28
0.0724	5.41	8.7	0.68	1.09
0.0622	4.47	8.7	0.67	1.28
0.0595	3.3	5.05	0.80	1.22
0.0585	$5 \cdot 2$	8.7	0.65	1.09
0.0482	$4 \cdot 3$	8.7	0.62	1.25
0.0346	4.41	8.7	0.57	1.12

In experiment 5, a yellow filter was employed to cut off the light of higher frequency.

The ratio quanta absorbed/molecules reacting was found to be independent of the light intensity over a range 1 to 6. It was also shown that an intermittent exposure produced the same effect as an equivalent continuous one.

Chlorine peroxide dissolves in water to give a yellow solution which is photochemically sensitive. Popper (Annalen, 1885, 227, 161; 231, 137) has shown, however, that the decomposition in sunlight is complex, and has represented it by the equation

18ClO₂ + 9H₂O \rightarrow 13HClO₃ + 3O₂ + 5HCl.

The reaction was therefore not studied.

Chlorine Monoxide Solutions.

Gaseous chlorine monoxide was found to decompose slowly in light by its discoverer (Balard, Ann. Chim. Phys., 1834, 57, 225), although Garzarolli, Thurnlack, and Schackerl (Annalen, 1885, 230, 273) reported only inappreciable decomposition after fifteen minutes' exposure to sunlight. Solutions of the gas in carbon tetrachloride undergo the stoicheiometric decomposition in light

$$2\text{Cl}_2\text{O} \longrightarrow 2\text{Cl}_2 + \text{O}_2.$$

It was found unnecessary to prepare the gaseous substance. Dry solutions of chlorine in carbon tetrachloride react quickly and

quantitatively with yellow precipitated mercuric oxide to give brown solutions of chlorine monoxide. The absorption spectrum of the solutions consists of a broad indefinite band in the blue and violet, quite different from that of solutions of chlorine peroxide (compare results for the gases, Kayser, "Handbuch der Spectroscopie," 1905, Vol. III, p. 366).

The solutions were dried with phosphoric oxide before being used. Analysis was carried out by running the liquid into excess of potassium iodide solution, acidified with a known amount of standard acid, titrating the iodine liberated, and then titrating the excess of acid, using methyl-orange as an indicator. The reactions involved are

 $\begin{array}{l} \mathrm{Cl_2O} + \mathrm{H_2O} + 4\mathrm{I'} \longrightarrow 2\mathrm{Cl'} + 2\mathrm{OH'} + 4\mathrm{I} \\ \mathrm{Cl_2} + 2\mathrm{I'} \longrightarrow 2\mathrm{Cl'} + 2\mathrm{I}. \end{array}$

Summary of Results.—

	posed
0.145 4.4 8.7 0.60 1.18	
0.140 4.03 8.7 0.585 1.24	
0.134 4.91 8.7 0.55 0.98	
0.112 4.14 8.7 0.49 1.03	
0.110 4.04 8.7 0.48 1.04	
0.109 3.55 8.7 0.47 1.15	
0.0855 3.06 8.7 0.42 1.20	

Nitrogen Trichloride Solutions.

Hentschel (*Ber.*, 1897, **30**, 1434) showed that nitrogen chloride, dissolved in various organic liquids, was decomposed by light, usually with formation of chlorination products of the liquids. In carbon tetrachloride, the decomposition is simple:

 $2\mathrm{NCl}_3 \longrightarrow \mathrm{N}_2 + 3\mathrm{Cl}_2.$

Solutions were prepared by shaking carbon tetrachloride containing chlorine with concentrated ammonium sulphate solutions, and were dried with phosphoric oxide. In colour, they resemble solutions of chlorine (Chapman, T., 1909, 95, 138). The light absorbed was small, making measurements inaccurate. Analyses according to the method of Dowell and Bray (J. Amer. Chem. Soc., 1917, 39, 896) yielded average ratios Cl/N of 3.5. The nitrogen chloride was estimated by running the solutions into concentrated sodium sulphite, and distilling off the ammonia into standard acid. The measurements are unsatisfactory because the amount of decomposition appeared only as a small difference.

and

Summary of Results.---

Conc. of NCl ₃ in gram-mol.	Molecules decomposed per sec. \times 10-16	Quanta per sec. in radiation	Mean absorp-	Quanta absorbed
0.43	13.7	8·7	0.43	0.27
0.316	4.8	8·7	0.28	0.508
0·290	$2.13 \\ 4.5$	8·7	0-29	1·18
0·227		8·7	0-308	0·595

The results seem to indicate that more than one molecule is decomposed for each quantum absorbed.

Discussion.

These results are of a preliminary character owing to the sources of error in the apparatus employed. They are, however, of sufficient accuracy to justify the raising of the question whether real unimolecular decompositions are ever found (compare Lowry, Trans. Faraday Soc., 1922, 596). In the case of thermal reactions, it is remarkable that only two possibly unimolecular reactions in the gaseous state (where complications due to solvent cannot occur) are known; the decomposition of phosphine at high temperatures (Trautz and Bhandarkar, Z. anorg. Chem., 1919, 106, 95) and the decomposition of nitrogen pentoxide (Daniels and Johnston, J. Amer. Chem. Soc., 1921, 43, 53). Even in these cases the evidence is scarcely conclusive. The measurements with phosphine are extremely inaccurate, and the rigorous criterion of the effect of change of pressure does not seem to have been applied, whilst the unimolecular mechanism of the nitrogen pentoxide decomposition has been criticised by the investigators themselves (J. Amer. Chem. Soc., 1922, 44, 2402). Almost all photochemical reactions exhibit complications of varying degrees of obscurity, and the only guide is that radiant energy must be absorbed in quanta. It appears probable from the measurements in this paper that the photochemical decompositions of the oxides of chlorine are unimolecular, and that the views of Baly (see Trans. Faraday Soc., 1922, 588) and of Weigert (Z. physikal. Chem., 1922, 102, 416) are unnecessary for the explanation of these cases. The mechanism of the decomposition may be formulated

oxides of chlorine $+ h_{\nu} \rightarrow$ "activated" molecule.

These "activated" molecules then largely decompose by a "dark" reaction. If this is so, then the unimolecular decomposition of the "activated" molecule would be expected to *evolve* heat; and this enables the mechanism to be discussed. The energy in violet light corresponds with 65,000 cals. per gram-molecule. The other

heat data available are only very approximate, and apply to the gaseous substances. In the dissolved state, the unknown heats of solution must be reckoned with, but it is unlikely that these will be large enough to invalidate the general results of the reasoning. Taking as rough approximations

$$2\text{Cl}_2\text{O} \longrightarrow 2\text{Cl}_2 + \text{O}_2 + 32,000 \text{ cals.}$$

 $2\text{Cl}_2 \longrightarrow \text{Cl}_2 + 2\text{O}_2 + 50,000 \text{ cals.} \text{ (estimated)},$

and the heats of dissociation of chlorine and oxygen as 100,000 cals. and 150,000 cals., respectively, we obtain for the hypothetical thermal reactions

$Cl_2O \longrightarrow Cl + Cl +$	0 - 159,000 cals	s	•		(1)
$Cl_2 O \rightarrow Cl_2 + O -$	- 59,000 cals.				(2)
$Clo_2 \rightarrow Cl + 0 +$	O - 175,000 cals				(3)
$ClO_2 \rightarrow Cl + O_2 -$	- 25,000 cals				(4)

The only reactions possible to a molecule activated to the extent of 65,000 cals. are (2) and (4).

In the case of the decomposition of nitrogen trichloride, taking

$$2\mathrm{NCl}_3 \longrightarrow \mathrm{N}_2 + 3\mathrm{Cl}_2 + 77,000$$
 cals.,

even the reaction

$$NCl_3 \rightarrow N + Cl_2 + Cl_3$$

is not possible in violet light if the heat of dissociation of nitrogen is more than 110,000 cals., as is probable. The assumption that this decomposition is not unimolecular, but that the activated molecule attacks an unactivated one, would agree with the rather unsatisfactory experimental results so far obtained. This reaction is being further studied.

The results obtained in this investigation are not considered sufficiently precise to say whether in obtaining the ratio quanta absorbed/molecules reacting the energy should be calculated in quanta at the frequencies actually absorbed, as appears probable, or at the frequency of the head of the band, as has been suggested (Lewis, "Physical Chemistry," 1919, Vol. III, p. 137).

If the constant frequency difference bands in the absorption spectrum of chlorine peroxide solutions are due to the superposition of rotational quanta on a vibrational quantum, such a decision would throw light on the interchanges between the various kinds of energy within the molecule.

Summary.

1. The photochemical decomposition of carbon tetrachloride solutions of chlorine peroxide and of chlorine monoxide under the influence of violet light appears to agree with the law of the photochemical equivalence. Solutions of nitrogen trichloride in similar circumstances give less certain results not far removed from the requirements of the law.

2. The mechanism of the photochemical decomposition has been discussed.

The thanks of the author are due to the Research Fund Committee of the Chemical Society for a grant which partly defrayed the expenses of the work.

PHYSICAL CHEMICAL LABORATORY, BALLIOL AND TRINITY COLLEGES, OXFORD.

[Received, March 13th, 1923.]