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PRIMARY DECOMPOSITION OF MOLECULES IN PHOTOCHEMICAL REACTIONS

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Introduction

Excited atoms and molecules produced by the primary action of the absorbed light have been found to be effective in stimulating photochemical changes in a number of photochemical reactions. When excited atoms or molecules are produced by the absorption of light, the absorption spectrum of the gas consists of lines or bands, respectively.

Recently it has been found that not all absorbers in photochemical reactions have line or band spectra. In fact some exhibit continuous absorption. Some writers have concluded that if the absorption spectrum of a diatomic molecule is truly continuous, the molecule is disrupted or decomposed into atoms when the frequency of the absorbed radiation is not great enough to produce ionization. Those photochemical reactions in which the absorber molecule has a continuous spectrum in the region of the spectrum under investigation, and consequently those in which the primary action of the light decomposes the molecule into atoms, have been called primary decomposition photochemical reactions in contrast to the excited atom or molecule types.

It is pointed out in this paper that a given photochemical reaction may belong to the excited molecule type in one region of the spectrum and to the primary decomposition type in another region of the spectrum; also that the quantum efficiency of the primary decomposition type is independent of the wave length and pressure, whereas it is not independent in the excited atom or molecule types.

Historical

Einstein's Law of Photochemical Equivalence, when tested by comparing the number of molecules which react with the quanta of radiation absorbed, appears to have been violated[1] in the majority of reactions which have been quantitatively studied. In the abnormally low yields the absorbed light energy may lose its effectiveness by fluorescence or ineffective collisions. Abnormally high yields may be attributed to chain reactions. While secondary reactions are of fundamental importance, it is wished to restrict the discussion primarily to the primary action of the light.

It is now accepted as fact that band spectra are attributed to change in rotational or vibrational or electronic energy levels or a combination of these changes in the molecules. On this basis Stern and Volmer[2] have taken issue with Warburg's[3] assumption that gaseous hydrogen bromide and hydrogen iodide are decomposed into atoms as a primary action of ultraviolet light. Moreover, they suggested that the hydrogen halide molecule is first excited by the ultraviolet light and that a collision of the excited molecule with a normal molecule produces a hydrogen and a halide molecule. More recently Franck[4] and Bodenstein[1] have also postulated that in general the primary action of light in photochemical reactions produces an excited molecule. Mulliken[5] assumed that iodine vapor in the visible spectrum is dissociated into atoms by the absorption of light in a region of continuous absorption. The reason given for this assumption is that in its absorption spectrum the vibration frequency of the atoms in the molecule approaches zero and that the band absorption spectrum in this region of the spectrum merges into a region of continuous absorption. In addition Franck[4] and Dymond[6] have observed that the absorption of light by the iodine molecule in the region of continuous absorption produces no fluorescence. With this additional evidence, Franck[4] asserts that the halogens are dissociated into atoms by the absorption of light in the region of continuous absorption. He also states that one of the dissociated atoms must be excited, inasmuch as the threshold value for the spectroscopic energy of dissociation is greater than the thermochemical value. Birge[7] and his associates have found that the absorption spectrum of oxygen is similar to that of iodine. In addition they have been able to calculate heats of dissociation of molecules from vibrational energy terms of band spectra data.

Tingey and Gerke[8] have made observations on the ultraviolet absorption spectra of hydrogen bromide and hydrogen iodide during photochemical

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[1] Bodenstein, *Trans. Faraday Soc.*, **21**, Part 3 (1925).

[2] Stern and Volmer, *Z. Wiss. Phot.*, **19**, 275 (1920).

[3] Warburg, *Sitzb. preuss. Akad. Wiss.*, 314 (1916); 300 (1918).

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

[5] Mulliken, *Phys. Rev.*, **25**, 509 (1925).

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

[7] Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

[8] Tingey and Gerke, THIS JOURNAL, **48**, 1836 (1926).

decomposition. These spectra were found to be continuous. It was concluded that these molecules were dissociated into atoms by the primary action of the light.

Additional examples of photochemical reactions will be found in Table I, in which the absorption spectra indicate that the primary action of the light is the dissociation of the molecules. Examples of the excited molecule class for which the spectroscopic data exist also will be listed in Table I.

The first class listed in Table I is called the "excited reactant" class, in which molecules are excited by the primary action of light absorption. Then by a collision the excited reactant molecule produces a photochemical reaction. The second class is called the "excited sensitizer" class, in which the radiation is absorbed by the sensitizer or catalyzer. This excited sensitizer then by a collision with the reactants utilizes this absorbed energy in producing photochemical change between reactants. The third class listed in Table I is called the "primary decomposition" class, in which the primary action of the absorbed light by the reactant is to produce decomposition of the reactant or sensitizer. It is stated whether great care was taken to remove traces of moisture. In those reactions in which heat is absorbed, the photochemical efficiency is usually low. In the exothermal reactions it is possible that the photochemical efficiency may become very great, especially in those reactions where traces of water are present. In this table it is noticed that there are very few exothermal reactions which are listed as reactions with secondary spontaneous chain reactions. This is due to the absence of data on the photochemical efficiency of these reactions in which water has been excluded.

TABLE I

PHOTOCHEMICAL REACTIONS

Reaction	Absorbing reactant or sensitizer	Type of abs. spectrum	Wave length of active radiation, Å.	No. of quanta of radiation abs. per mol. of reactant	Sign of heat effect of Col. 1 reaction
Excited reactant					
$O_2 = {}^2/_3O_3$[9,10,11,12]	O_2	Band[13]	1970–1756[13,14]	1.04–3.42[11]	Endothermic
$NH_3 = {}^1/_2N_2 + {}^3/_2H_2$[15]	NH_3	Band[14]	2260–1515[14,16]	2–10[15,17]	Endothermic
$O_3 = {}^3/_2O_2$[18]	O_3	Band	6700[18] and U.v.[19]	....	Exothermic
$H_2 + {}^1/_2O_2 = H_2O$ (dry)[12]	O_2	Band	1970–1756[14]	....	Exothermic
$CO + {}^1/_2O_2 = CO_2$ (dry)	O_2	Band	1970–1756[14]	....	Exothermic

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[9] Lenard, *Ann. Physik*, **1,** 480 (1900).

[10] Goldstein, *Ber.*, **36,** 3042 (1913).

[11] Warburg, *Sitzb. preuss. Akad. Wiss.*, 216 (1912); 644 (1913); 872 (1914).

[12] Tram, *Z. physik. Chem.*, **105,** 356 (1923).

[13] Kayser, "Handbuch der Spectroscopie," **3,** 360 (1905).

[14] Leifson, *Astrophys. J.*, **43,** 73 (1926).

[15] Warburg, *Sitzb. preuss. Akad. Wiss.*, 746 (1911); 216 (1912).

[16] Ferriers, *Compt. rend.*, **178,** 202 (1924).

[17] Kuhn, *ibid.*, **177,** 956 (1923).

[18] Griffith and Shutt, *J. Chem. Soc.*, **119,** 1948 (1921).

[19] Fabry, *J. Math. Phys.*, **4,** 1 (1925).

TABLE I (*Concluded*)

Reaction	Absorbing reactant or sensitizer	Type of abs. spectrum	Wave length of active radiation, Å.	No. of quanta of radiation abs. per mol. of reactant	Sign of heat effect of Col. 1 reaction
$CH_3COH + {}^1/_2O_2 =$					
CH_3COOH[20]	CH_3COH	Band	2800–2350[20]	....	Exothermic
Excited sensitizer					
$H_2 = 2H$[21]	Hg	Line	2536	....	Endothermic
$O_3 = {}^3/_2O_2$[22]	Hg	Line	2536	....	Exothermic
$H_2 + {}^1/_2O_2 = H_2O$[23]	Hg	Line	2536	....	Exothermic
$N_2O_5 = N_2O_4 + {}^1/_2O_2$[24]	NO_2-N_2O_4[24]	Band[25]	4600–4000[24]	....	Very small
${}^3/_2H_2 + {}^1/_2N_2 = NH_3$[26,27]	Hg	Line	2536	....	Exothermic
$H_2 + C_2H_4 = C_2H_6$[27]	Hg	Line	2536	....	Exothermic
$H_2 + CO = HCOH$[27]	Hg	Line	2536	....	Very small
$H_2 + CO_2 = H_2 + CO_2$[27]	Hg	Line	2536	....	Endothermic
$O_2 = {}^2/_3O_3$[28]	Hg	Line	2536	....	Endothermic
Primary decomposition					
$HCl = {}^1/_2H_2 + {}^1/_2Cl_2$ (dry)[29]	HCl	Cont.[14]	2640–1800[8]	....	
$HBr = {}^1/_2H_2 + {}^1/_2Br_2$					Endothermic
(dry)[29,3,8]	HBr	Cont.[8]	3320–1800[8]	0.521–0.502	Endothermic
$HI = {}^1/_2H_2 + {}^1/_2I_2$ (dry)[29,3,8]	HI	Cont.[8]	2600–1800[20]	0.526–0.495	Endothermic
$H_2S = H_2 + {}^1/xS_x$					
(dry)[30,31,32]	H_2S	Cont.[20]	2300–1800[20]	....	Very small
$CH_3COH = CH_4 + CO$[20]	CH_3COH	Cont.[20]	2300–1800[20]	....	Endothermic
$I_2 = I + I_{(ex)}$[4,5]	I_2	Cont.[4,6,25]	5000[4,6,25]	....	Endothermic
$Br_2 = Br + Br_{(ex)}$[4]	Br_2	Cont.[4,25]	5200[25]	....	Endothermic
$Cl_2 = Cl + Cl_{(ex)}$[4]	Cl_2	Cont.[4,20,25]	4800[20,25]	....	Endothermic
$Cl_2 + H_2 = 2HCl$ (dry)[33,34,12]	Cl_2	Cont.	3000[33]	chain[35]	Exothermic
$Cl_2 + CO = COCl_2$ (dry)[12]	Cl_2	Cont.	Ultraviolet[12]	....	Exothermic
$Cl_2 + SO_2 = SO_2Cl_2$ (dry)[12]	Cl_2	Cont.	Ultraviolet[12]	....	Exothermic
$O_2 = 2O$[7]	O_2	Cont.	1750[14]	....	Endothermic
$O_2 = {}^2/_3O_3$[36]	O_2	Cont.	1750[36,14]	....	Endothermic
$O_3 = {}^3/_2O_2$[37]	O_3-Cl_2	Cont.	4360 and 4060[37]	0.54–0.43[37]	Exothermic
$O_3 = {}^3/_2O_2$[37]	O_3-Br_2	Cont.	4360 and 4060[37]	0.035–0.029[37]	Exothermic

It is possible to have a complex reaction in which the rate of the reaction is the sum of the separate rates which correspond to the classes listed above. Thus in Table I the decomposition of ozone in the presence of chlorine

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[20] Henri, "Structure des Molecules," J. Hermann, Librairie Scientifique, 6, Rue de la Sorbonne, Paris, **1925**, p. 100.

[21] Franck and Cario, *Z. Physik*, **11**, 161 (1924).

[22] Weigert, *Z. physik. Chem.*, **106**, 407 (1923).

[23] Marshall, *J. Phys. Chem.*, **30**, 34 (1926).

[24] Daniels and Johnston, THIS JOURNAL, **43**, 72 (1921).

[25] Wood, "Physical Optics," The Macmillan Company, New York, **1923**.

[26] Noyes, THIS JOURNAL, **47**, 1003 (1925).

[27] Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

[28] Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).

[29] Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916).

[30] Bertholet and Gaudechon, *Compt. rend.*, **150**, 1517 (1910).

[31] Smits and Aten, *Z. Elektrochem.*, **16**, 264 (1910).

[32] Teves, Unpublished.

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

[34] Cohn, *Ber.*, **56**, 696 (1923).

[35] Marshall, *J. Phys. Chem.*, **29**, 1453 (1925).

[36] Born and Gerlach, *Z. Physik*, **5**, 433 (1921).

[37] Bonhöffer, *ibid.*, **13**, 94 (1923).

as a sensitizer is the sum of the rate of decomposition of ozone caused by its own absorption of light and the rate of decomposition caused by the absorption of light by the catalyzer, chlorine. The decomposition of ozone in the presence of chlorine or bromine, as listed in Table I, is principally sensitization by primary decomposition. When more reactions of this type are investigated, it may be convenient to subdivide primary decomposition photochemical reactions into the reactant and sensitizer classes.[38]

Einstein's Law of Photochemical Equivalence

Einstein's law of photochemical equivalence appears to have been found wanting in all of the "excited reactant" and "excited sensitizer" photochemical reactions in Table I. The reason which has been given for the failure of this law lies in the possibility that the excited reactant or sensitizer may re-radiate the absorbed radiation as fluorescent radiation or lose it by collisions which are ineffective in producing photochemical reactions. On the other hand the examples of the "primary decomposition" class in Table I which have been quantitatively investigated are in complete harmony with Einstein's law. The photolyses of hydrogen bromide and hydrogen iodide have been quantitatively investigated as a function of temperature, wave length, pressure, inert gas and in the liquid state with the universal result that two molecules are decomposed per quantum of absorbed radiation.[1,39]

While the data are very complete for these two reactions, data on other reactions should be available before it would be certain that only "primary decomposition" photochemical reactions obey Einstein's law. Moreover, it would seem reasonable that every quantum of absorbed light which decomposes a molecule into atoms has a better chance of producing secondary reactions than one which produces an excited molecule in which one of the electrons is temporarily lifted to a higher energy level.

The Halogens.—In the band absorption spectra of the halogens the vibration frequency approaches zero and a region of continuous absorption sets in. Mulliken[5] has assumed that it was possible that the halogens were decomposed into atoms in the region of continuous absorption. Franck[4] and Dymond[6] have assumed that the halogens are decomposed into a normal atom and an excited atom because the radiant energy is greater than the thermochemical heat of decomposition. They also state that the iodine fluorescence cannot be excited by absorption of the light

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[38] The writer is indebted to Professor S. C. Lind for this suggestion.

[39] It is not to be expected that all reactions of this class should have the same photochemical efficiency since, in general, secondary reactions are to be expected which may be different for different reactions. Investigation of other photochemical reactions with continuous absorption spectra will be interesting from this point of view. It seems possible that the photolysis of hydrogen bromide and hydrogen iodide should be very useful for the counting of quanta in a given beam in ultraviolet light.

in the continuous region. Accordingly, the class to which a photochemical reaction in which the halogen is the absorber belongs depends upon whether the wave length of light is in the region of band or continuous absorption.

The Halogen Hydrides.—The photographs of the absorption spectra of hydrogen chloride, bromide and iodide have been found to be continuous in structure.[14,8] Tingey and Gerke[8] have discussed the possibility as to whether the structure is apparently or actually continuous. It was concluded that the structure must be actually continuous if the spacing of the vibrational energy levels for the hypothetical electronic excited molecules would be approximately equal to those of the normal molecule. If it is granted that these absorption spectra are actually continuous, then it seems necessary that the primary action of the light produces a splitting of the molecule into two parts, which are presumably atoms. This assumption has in its support that no emission band spectra[40] corresponding to uni-univalent polar molecules have ever been observed.

With respect to the photochemical formation of the hydrogen chloride by the absorption of light by chlorine it is necessary to mention that the absorption of light in the continuous region and beginning with 3000 Å.[33] has been found to be effective when the gases are dry. In the presence of traces of water vapor wave lengths in the region of band absorption in the visible are also effective. Consequently the photochemical formation of hydrogen chloride in the absence of impurities is listed in the primary decomposition class. Moreover, this reaction in the presence of water vapor is not listed at all because the facts are not clear as to the role of the water vapor. For example, it has been found that in the case of the formation of hydrogen chloride one quantum of visible light would produce about a million molecules of hydrogen chloride,[41] whereas it[12,33] has been found that the reaction hardly proceeded at all in the visible region where the reaction mixture was carefully freed from water.

Oxygen.—The asborption spectrum of oxygen has been found to be similar to those of the halogens by the recent measurements of Leifson.[14] In the far quartz and the near fluorite ultraviolet regions are the absorption bands of oxygen which at shorter wave lengths merge into a region of continuous absorption. Birge and Sponer[7] attribute this continuous absorption to a dissociation of the molecule. It will be interesting to compare the photochemical activity of oxygen in the region of band and continuous absorption. Born and Gerlach[36] observed that the production of ozone was very great in the region of continuous absorption and that it seemed to fall off abruptly at greater wave lengths where band absorption began. The careful quantitative experiments of Warburg[11] in the region of band absorption show that oxygen forms ozone, but that 1.04 to 3.04

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[40] Mulliken, *Phys. Rev.*, **26**, 1 (1925).

[41] Bodenstein, *Z. physik. Chem.*, **85**, 351 (1913).

quanta are necessary to decompose one molecule of oxygen. This efficiency depends upon the wave length and the pressure. The formation of ozone is an example of both the "excited reactant" and "primary decomposition" types of photochemical reaction, depending upon whether the absorption spectrum consists of bands or is continuous in structure.

Ammonia.—The nature of the photochemical decomposition of ammonia has been uncertain, due to the fact that no definite conclusion could be drawn as to whether the absorption spectra were bands or continuous in structure. Examination of Leifson's recent data,[14] however, shows that the structure consists of bands throughout the whole region of absorption. The decomposition of ammonia, therefore, belongs to the "excited reactant" type. It is interesting to note that the photochemical efficiency, which was quantitatively studied by Warburg[15] and by Kuhn[17] with monochromatic light depends upon the wave length of light.

Summary

The recent data on absorption spectra of gases entering into photochemical reaction, together with the older data, have made possible an extended study of the nature of the primary action of the absorbed light. In several cases band or line spectra have been observed for the absorbers which definitely classify these photochemical reactions into two widely known types of photochemical action which have been called in this paper the "excited reactant" and "excited sensitizer" types. In other cases not band spectra but continuous spectra were observed. Some authors have concluded as a necessary consequence of the most recent developments of the quantum theory of molecular spectra that the primary action of light in these cases is a dissociation of the molecule. Several examples of this class, which have been called the "primary decomposition" type in this paper, have been collected and compared with examples of the "excited reactant" and "excited sensitizer" types of photochemical reaction.

The quantum efficiencies of photochemical reactions as measured by the number of molecules which react per quantum of light absorbed are in accord with the suggestion; the chance for stimulation of photochemical action by excited molecules or atoms is not as great as by atoms produced from molecules by the primary action of the absorbed radiation.[42]

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[42] Since the manuscript was first written the writer has noted the interesting articles by Bonhoeffer and Steiner, *Z. physik. Chem.*, **122**, 287 (1926), on the continuous absorption in hydrogen iodide vapor and by Lewis, *Nature*, **119**, 493 (1927), on the constancy of the quantum yields on the photolysis of hydrogen iodide at very low pressures, which support the primary decomposition mechanism for those photochemical reactions with continuous absorption spectra.