THE UTILIZATION OF THE SOLAR ENERGY THROUGH PHOTOCHEMICAL REACTIONS

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Many molecules and atoms absorb light and as a result undergo chemical change. Since light is one form of energy, light absorbed by a molecule results in an increase in energy of the absorbing molecule. Certain chemical changes may occur involving the molecule activated by light. If the reactions of the excited molecule are less exothermic than the energy of the light absorbed, the products of the light-initiated reaction will have a greater chemical energy than the reactants, and the over-all reaction will have resulted in the conversion of light energy into chemical energy. The trapping of the sun's light-energy by non-biological photochemical processes of this kind has been a hope of scientists for a great number of years. It is the purpose of the paper to summarize some of the fundamental considerations and problems involved in this study and to indicate the present status of research in this field.

LIGHT ABSORPTION BY MOLECULES AND ATOMS

The absorption act.—Any molecule or atom absorbing a quantum of radiant energy of wave length λ is increased in energy E by an amount, $E = hc/\lambda$, where h is Planck's constant, and c is the velocity of light. The immediate result of the absorption of light in the visible or ultraviolet range ($\lambda = 7,000$ to about 1,000 Å.) is an electronic excitation of the molecule or atom.

Reactions of the excited molecule.—Experimentation has shown that only light of wave length less than about 7,000 Å. contains sufficient energy per quantum (greater than 41 kcal./mole of quanta) to effect most chemical changes, such as breaking bonds between atoms, etc. For the ordinary forms of matter exposed to the usual intensities of sunlight the absorption of more than one quantum of light per molecule is extremely improbable and does not occur usually; this is a consequence of the very short lifetimes of the excited molecules. Roughly

fifty percent of the solar radiant energy which we receive at the earth's surface has a wave length less than 7,000 Å. and is thus sufficiently energetic to produce chemical changes in an absorbing molecule. An increase in temperature of the absorbing molecules is the predominant result of the absorption of light which is greater than 7,000 Å. in wave length.

Some of the important modes of reaction of the light activated molecule include: (a) fluorescence (all, or more often, a part of the energy absorbed is emitted as light); (b) loss of the excitation energy by collisional deactivation; (c) dissociation of the molecule into simpler molecules or radicals (molecular fragments); (d) isomerization or molecular rearrangement; (e) a chemical reaction between an excited molecule and a normal molecule. The only change which results in a light absorbing system which involves only reactions (a) and/or (b) is an increase in the thermal energies of the molecules. The occurrence of reactions (c), (d), and (e) usually results in a chemical change in the system. If light energy is absorbed by a chemical system and reaction (a) does not occur exclusively, then the total energy of the chemical system is increased necessarily for every such system. The increase in energy is made manifest by an increase in thermal energy of the molecules in the system and by an increase in chemical energy from the formation of energy-rich products. For the purpose of light energy conversion to chemical energy and storage of this energy, only systems involving the formation of energy-rich products are important. In this discussion such reactions will be referred to as "endothermic" photochemical reactions.

"ENDOTHERMIC" PHOTOCHEMICAL REACTIONS

The ideal reaction.—An ideal photochemical reaction for the conversion of light energy into chemical energy may have the following characteristics. (a) The reactant molecules absorb strongly all radiation in the visible and ultraviolet. In other words, the reactant is black or dark in color. (b) A given chemical reaction follows the absorption of each quantum of light with perfect efficiency. Reactions of fluorescence and collisional deactivation are unimportant. (c) The over-all chemical change in the reaction system involves a large increase in free energy. (d) The products formed absorb no light in the visible or ultraviolet region; therefore they are colorless. (e) The exothermic reaction of the products to reform the reactants is extremely slow under ordinary conditions but this or some other reaction involving the products proceeds readily under special controlled conditions (e.g., at an elevated temperature or in a battery) to liberate thermal or electrical energy.

A measure of the efficiency of energy conversion.—In our discussion of the "endothermic" photochemical reactions it will be useful to define and use a quantity, Q, which provides a measure of the percent efficiency of the light energy conversion to chemical energy.

$$Q = (100) \ (\Delta F°_{298}) \ (\Phi_A)/E\lambda,$$

where $\Delta F°_{298}$ is the standard free energy increase for the over-all chemical reaction (kcal./mole of a given product A formed), Φ_A is the quantum yield of the given product A (molecules of A formed/quantum of light absorbed by the reactant), and $E\lambda$ is the energy of the absorbed light of wave length λ ($E\lambda$ in kcal./mole = $2.86 \times 10^5/\lambda$ in Å.). Q can give at best only an approximate indication of the efficiency of energy conversion for several reasons: (a) the photochemical reactions for which data are available were not studied with reactants and products in concentrations corresponding to the reference states used for $\Delta F°_{298}$ calculations; (b) the quantum yield data are usually maximum values obtained only under special conditions (certain wave length region, low percentage reaction, etc.); (c) the effects of product interference by absorption and subsequent decomposition or reaction are not considered; (d) a great many "endothermic" photochemical

reactions are reversible; a definite photostationary concentration of reactants and products is reached, and then concentrations remain unchanged for a given temperature, light intensity, and initial concentration of reactants or products. The values of the photostationary concentrations are important in determining the usefulness of a given "endothermic" photochemical reaction for energy conversion. Unfortunately this type of data is not available for most reactions. The factors stated cause the estimate of efficiency of energy conversion, Q, to be higher than actually obtainable experimentally. Regardless of the approximate nature of Q we will find that it is a useful guide to our discussion.

Photosynthesis in vitro.—Many attempts have been made to accomplish photosynthesis in the laboratory without the help of living cells. A general over-all reaction which will serve to illustrate photosynthesis may be written: $nH_2O + nCO_2 \longrightarrow (CH_2O)n + nO_2$, where n is some whole number. The reaction is highly endothermic; about 110 kcal. of energy is evolved when the organic product material containing one gram atom of carbon is burned in air. Energy considerations and the transparency of water and carbon dioxide to all wave lengths of visible and near ultraviolet light make impossible the occurrence of this reaction involving only pure water, carbon dioxide, and sunlight. The very short ultraviolet wave lengths (where absorption and energies are more

TABLE 1

Some far ultraviolet "endothermic" photochemical reactions.

OVER-ALL CHEMICAL REACTION	EFFECTIVE WAVE LENGTHS, Å	QUANTUM YIELD (product)	$\Delta F°_{298}$ kcal./ mole	Q PERCENT EFFICIENCY	INVESTIGATORS
(1) $3/2\ O_2 \longrightarrow O_3$	<1751 (weak absorption)	2.0 (O_3)	32.4	40.5	Warburg (1914) Vaughan, Noyes (1930)
	2070	2.0		47.0	
	2537	1.1		31.8	
(2) $CO_2 \longrightarrow CO + \frac{1}{2} O_2$	<1692	1.0 (CO)	61.4	36.4	Groth (1937)
(3) $H_2O \longrightarrow H_2 + \frac{1}{2} O_2$	<1800	(small)	54.5		Groth, Suess (1938) Terenin, Neuimin (1934)
(4) $CO + H_2 \longrightarrow CH_2O$	<1470	0.5(CH_2O)	6.6	1.7	Groth (1937)
(5) $NH_3 \longrightarrow \frac{1}{2} N_2H_4 + \frac{1}{2} H_2$	<2138	0.5(H_2)	17.1 ($\Delta H°_{298}$)	12.8	Review of work by Noyes, Leighton (1941)
(6) $CH_4 \longrightarrow \frac{1}{2}H_2 + \frac{1}{2} C_2H_6$ or	<1450				Groth (1937)
	1295	0.5(H_2)	6.9	3.1	Groth, Laudenklos (1936)
$CH_4 \longrightarrow H_2 + \frac{1}{2} C_2H_4$			18.4	4.2	Leighton, Steiner (1936)

favorable for the reaction) may cause the occurrence of this or related reactions, but its occurrence is questionable even under these conditions (Rabinowitch, 1945). It is not inconceivable that we may be able to realize the reaction *in vitro* through the proper choice of sensitizer, catalysts, etc., after our knowledge of the mechanism of photosynthesis *in vivo* has been greatly increased.

Known "endothermic" photochemical reactions.—The inexperienced investigator in this field may be surprised to find that the great majority of known photochemical reactions are accompanied by an over-all decrease in free energy; i.e., a normally slow, exothermic reaction is promoted by light, and the energy of the absorbed light plus that due to the exothermal nature of the reaction ultimately appears as an increase in velocity of the product molecules. However, there are a relatively small number of "endothermic" photochemical reactions which have been reported. It is probably unnecessary to point out that no system is now known which is at all comparable to the "ideal reaction" described in a preceding section. The "endothermic" photochemical reactions may be divided

into two groups for the purposes of our discussion: the reactions occurring on the absorption of the far ultraviolet light ($\lambda < 2,500$Å.), and those reactions occurring on the absorption of visible or the near ultraviolet radiation.

The far ultraviolet "endothermic" photochemical reactions.—A few of the "endothermic" photochemical reactions which occur on absorption of light in the far ultraviolet are summarized in table 1. Only the over-all chemical change which takes place is listed in each case; for our very limited considerations it is an unnecessary complication to describe the detailed mechanism of the reaction steps which lead to the over-all reactions. The very short wave lengths of light which promote these chemical changes are absent in sunlight striking the earth as a result of the occurrence of some of these and other photochemical reactions in the upper atmosphere of the earth. The distribution of solar radiant energy reaching the earth's surface at Cleveland on a clear summer day when the atmospheric pressure is 1.07 atm. has been calculated by Forsythe and Christison (1930). A portion of their data is reprinted in table 2. There are minor variations in this distribution with changes in season, pressure, etc. Since light energy must be absorbed before a chemical change can be effected photochemically, the direct occurrence of the reactions of table 1 in sunlight incident at the earth's surface is impossible. However it is probable that these and other "endothermic" photochemical reactions were important in the prebiological chemistry of the earth.

TABLE 2

Distribution of radiant energy from the sun on the earth's surface at Cleveland*

WAVE LENGTH REGION, Å.	PERCENTAGE OF THE TOTAL ENERGY
2900–3100	0.019
Less than 3250	0.21
Less than 3500	1.0
Less than 4000	3.8
4000–7600	43.9
Greater than 7600	52.3

* Forsythe, W. E., and F. Christison (1930).

The near ultraviolet and visible "endothermic" photochemical reactions.—In table 3 several "endothermic" photochemical reactions which are initiated by the absorption of visible or ultraviolet light are summarized. Reactions (7), (8), (9), (10), and (15a) occur only in the ultraviolet region of light; since this region is practically absent from sunlight (table 2), these reactions will remain unimportant for energy conversion on the earth unless some photochemical sensitizer for the longer wave lengths is found for these systems.

It should be noted that the possibility exists of extending the useful wave length region of a given reaction to a position which is more compatible with the energy distribution of the sun. For example, Blacet (1952) has proposed tentatively that ozone formation [reaction (1) of table 1] at the earth's surface may result from the primary absorption of light by nitrogen dioxide (effective absorption region, $\lambda < 4,350$ Å.) according to the following sequence of reactions:

$$NO_2 + h\nu \longrightarrow NO + O$$
$$O + O_2 \dashrightarrow O_3$$
$$NO + O_2 \longrightarrow NO_3$$
$$NO_3 + O_2 \longrightarrow NO_2 + O_3$$
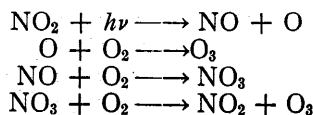
($h\nu$ represents the energy of a quantum of light of frequency, ν.)   If these reactions occur, the over-all change resulting from light absorption by the nitrogen dioxide is given by: $3O_2 \longrightarrow 2O_3$.   Thus a change which is effected as a result of direct light absorption by a reactant only at the very short wave lengths may be made to occur indirectly by a sequence of reactions initiated by visible light absorption by a sensitizer.

TABLE 3

Some ultraviolet and visible "endothermic" photochemical reactions

Over-All Chemical Reaction	Effective Wave Lengths, Å.	Quantum Yield (product)	$\Delta F°_{298}$, kcal./ mole	Q Percent Efficiency	Investigators
(7) $HBr \longrightarrow \frac{1}{2} Br_2 + \frac{1}{2} H_2$	<2537	1.0 (Br₂)	12.5	22.2	Warburg (1916)
	2090	1.0		18.3	
(8) $SO_3 \longrightarrow \frac{1}{2} O_2 + SO_2$	<2760	(small)	16.2		Kornfeld (1937)
(9) $COCl_2 \longrightarrow CO + Cl_2$	<2750	0.9(CO)	16.3	14.0	Montgomery and
	2537			13.1	Rollefson (1934)
(10) $NO^-_3 \longrightarrow NO^-_2 + \frac{1}{2} O_2$	<3350	0.014(NO⁻₂)	18.0	0.20	Warburg (1918)
(water solution)	2804	0.024		0.42	Villars (1927)
	2700	0.07		1.2	
	2540	0.30		4.8	
(11) $NO_2 \longrightarrow NO + \frac{1}{2} O_2$	<4350	0.046(NO)	9.0	0.6	Dickinson, Baxter (1928)
	4050	0.36		4.6	
	3660	0.77		8.8	
(12) $NOCl \longrightarrow NO + \frac{1}{2} Cl_2$	<6370	2.0(NO)	4.9	21.8	Bowen, Sharp (1925)
	3650	2.0		12.5	Kistiakowsky (1930)
(13) $2Fe^{+2} + I^-_3 \longrightarrow 2Fe^{+3} + 3I^-$	<5460	2.0(Fe⁺³)	9.4	9.0	Kistiakowsky (1927)
(water solution)	3660			6.0	
(14) $I_2 + NO^-_2 + H_2O$	<5790				
$\longrightarrow NO^-_3 + 2HI$					
(water solution)	4360	0.1(NO⁻₃)	13.8	2.1	Durrant, *et al.*, (1938)
(15a) $Fe^{+2} + H_2O \longrightarrow \frac{1}{2} H_2 +$					
$Fe^{+3} + OH^-$	<2900	0.05(H₂)	36.2	3.7	Potterill, *et al.*, (1936)
(water solution)					
b) $Fe^{+2} + H^+ \longrightarrow Fe^{+3} +$					
$\frac{1}{2} H_2$ (HClO₄ solution)	2537	0.1(H₂)	17.1	3.0	Heidt, DesRoches
	(5900?)				(1952)
(16) 2 Anthracene $\longrightarrow$ Dianthracene	<3800		15.6		Weigert (1927)
(organic solution)	3660	0.25(Dian.)	($\Delta H°_{298}$)	5.0	
	3130	0.23		3.9	
(17a) $AgCl(s) \longrightarrow Ag(s) + \frac{1}{2} Cl_2$	<4050	1.0(Ag)	26.2	37.1	Luther (1899)
					Hartung (1922)
b) $AgBr(s) \longrightarrow Ag(s) + \frac{1}{2} Br_2$	<4600	1.0(Ag)	22.9	37.0	Hartung (1924)
c) $AgI(s) \longrightarrow Ag(s) + \frac{1}{2} I_2$	<4400	1.0(Ag)	15.8	24.3	Hartung (1926)
d) $AgCl + \frac{1}{4} H_2O \longrightarrow Ag +$					
$HCl + \frac{1}{8} O_2$	<4050	(1.0?)	23.2	(32.9)	Baur (1908)
(water suspension)					Baur, Rebmann (1921)
(18) $H_2O + \frac{1}{2} O_2 \longrightarrow H_2O_2$	<4000		25		Baur, Neuweiler (1927)
(water suspension of ZnO)	3660	0.09(H₂O₂)		2.9	Kettering Research
	3130	0.13		3.6	Group (1952)

There are few known gas phase reactions which offer promise as energy converters.   The reactions (11) and (12) have reasonably large Q values and fairly satisfactory absorption.   The reverse thermal reactions are termolecular in each case, but even so the rates of reaction are too rapid at ordinary pressures and temperatures to make practical the storage of the energy-rich products without separation.

A few homogeneous solution reactions appear to satisfy some of our requirements for the ideal "endothermic" photochemical reaction.   Reactions (13),

(14), and (15b) illustrate this type. One of the most promising of these is reaction (15b), although product absorption becomes serious at small percentages of conversion at some wave lengths. Preliminary results of Heidt and DesRoches (1952) have indicated that the evolution of hydrogen occurs even when the solution of iron salt in perchloric acid is exposed to yellow light.

The useful spectral range of reaction (16) is limited to wave lengths less than 3,800 Å. (less than two percent of the total sunlight energy), but at these wave lengths the conversion of anthracene to dianthracene may be effected quite efficiently and continuously without serious interference from light sensitive products; the slightly soluble dianthracene separates during exposure of a solution of anthracene in some organic solvents.

It appears that a very important contribution to the problem of light to chemical energy conversion has been made recently by Heidt (1951). He reported that a sensitized photodecomposition of water [reaction (3) of table 1] occurs in the perchloric acid solutions of ceric and cerous perchlorates. The efficiencies of this "endothermic" photochemical reaction were very low and only light of wave length 2,537 Å. was used in the experiments described. However, Heidt stated that no attempt has been made yet to increase this efficiency (by the proper choice of sensitizer concentration, etc.), and also it is logical to assume that wave lengths longer than 2,537 Å. which are absorbed by the cerium ions will be effective in promoting the reaction. The ease with which the energy rich products, hydrogen and oxygen, can be stored and used as a high energy fuel when desired adds to the great attractiveness of this system.

Several heterogeneous reactions involving solids are given in table 3. The silver halide decomposition reactions (17a), (17b), and (17c) which are important in photographic processes may prove useful as energy converters.

Hydrogen peroxide formation by reaction (18) involves the light activation of zinc oxide crystals suspended in a water solution. The absorption of zinc oxide limits the reaction to wave lengths comprising only four percent of the sunlight energy, and the light energy in the wave length region utilized is converted with relatively low efficiency. However, this system has an inherent appeal as an energy converter. It appears that the highly endothermic reaction (18) is promoted from readily available reactants; the energy rich product is transparent to sunlight; the product can be stored conveniently; and the reverse reaction of peroxide decomposition can be catalyzed at will to release energy. In view of these considerations, several detailed reinvestigations of this system have been initiated recently (Kettering Research Foundation, 1952).

SUMMARY

Although no ideal chemical reaction system for the conversion of the sun's radiant energy to chemical energy is now known, several reactions under study are sufficiently attractive to give encouragement and hope for a possible ultimate solution to this problem.

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