PHOTOCHEMISTRY deals with all reciprocal actions between chemical energy and light energy. Included, first of all, are chemical processes that proceed with evolution of energy in the form of light (chemiluminescence). The most familiar instance is the glowing that accompanies the autoxidation of yellow phosphorus. The reverse process is far more common, namely, the effecting of chemical changes by light. This is the real domain of photochemistry, because it has been found that many examples of the influence of light can be cited for almost all types of chemical reactions, no matter whether they involve inorganic or organic materials, and no matter what their state of aggregation.

The fundamental law (Grotthus, 1817), that holds for every photochemical reaction, states that only absorbed light can accomplish chemical changes; reflected or transmitted light is without effect. However, the absorption of light is only a necessary but not sufficient requirement for the initiation or acceleration of chemical processes. There are many cases in which light is absorbed without chemical change. On the other hand, it has long been known that if a chemical reaction is brought about by absorption of light, the extent of the change (after a certain induction period) is always proportional to the intensity of the incident and absorbed light. Furthermore, the wave length of the absorbed light is of decisive significance in photochemical reactions.

Although the connection between light and chemical changes had been established experimentally in numerous cases, the systematic studies and measurements, as well as a theoretical foundation, date from the application of the quantum theory (Planck, 1900). According to this theory, energy, no matter what its nature, is not evolved or absorbed gradually and continuously, but in elementary units (quanta). The introduction of the quantum theory into the course of photochemical reactions is expressed in the law of photochemical equivalence (Einstein, 1912). This states that each light quantum ($h\nu$) of the active light is taken up by one molecule or atom of the absorbing and photochemically active system. Accordingly, one gram molecule of the light-sensitive material reacts by taking up $6.10^{29}$ light quanta. The $h$ of the term $h\nu$ is a universal constant ($h = 6.54 \times 10^{-37}$ erg/sec); $\nu$ is the frequency of the light, i.e., the velocity divided by the wave length.

Complete validity of the law of photochemical equivalence would require that the quotient obtained by dividing the number of chemically altered molecules of the light-sensitive system by the number of light quanta absorbed equal unity. This quotient is called the quantum yield of a photochemical process. Actual determinations have shown that this requirement is exactly met in many cases. Frequently, however, it has been found that the quantum yield is much larger or smaller than 1. However, under fixed experimental conditions, the quantum yield of every photochemical process is a definite, reproducible, and characteristic figure.

A satisfactory explanation of the validity and also of the apparent deviations from the law of photochemical equivalence is obtained by considering those physical and chemical effects, which, through their succession and ensemble, condition the occurrence and extent of photochemical reactions.

If the Bohr theory of the structure of the atom is accepted, photochemical processes can be viewed as follows: The absorption of a light quantum causes an outer electron of an atom to shift into a higher quantum orbit, that is, into a level of greater energy. Accordingly, the absorption of light causes molecules or certain atoms of molecules to shift from a normal, non-reactive state into an energized and therefore more reactive condition. The taking up of light quanta is the primary process, essential to every chemical change due to the action of light. This purely physical process of taking up quanta can be formulated: $AB + h\nu \rightarrow AB^*$. In this expression, $AB$ is the normal molecule, $h\nu$ a light quantum of frequency $\nu$, and $AB^*$ the energized, activated molecule.

In the total photochemical reaction, the primary process is followed by secondary physical and chemical processes. These may be:

1. Reversion of the activated molecule to its normal condition with emission of energy in the form of heat, motion, or light:
   
   $$AB^* \rightarrow AB + h\nu$$

   The emission of light is fluorescence.

2. Reversion of the activated molecule into the
normal condition with transfer of energy to other molecules (sensitization):

\[ AB^* + M \rightarrow AB + M^* \]

The transfer of energy gained by absorption of light from activated molecules to molecules of other compounds, that of themselves are not activated in this same light, is known as photosensitization. The product \( M^* \) can participate in the secondary processes given under (3) to (6). Consequently, when sensitization occurs, the light-absorbing system is chemically unaltered at the completion of the process. It functions merely as a vehicle for the transfer of energy.

3. Dissociation of the activated (sensitized) molecule into radicals, atoms, or ions:

\[ AB^* \rightarrow A + B \]

4. Polymerization of the activated (sensitized) molecule with identical nonactivated molecules:

\[ AB^* + AB \rightarrow AB, \text{ etc.} \]

5. Inner-molecular rearrangements of the activated (sensitized) molecule to produce an isomer:

\[ AB^* \rightarrow BA \]

6. Direct or indirect chemical reactions:

(a) reactions of the activated (sensitized) molecule with other molecular species:

\[ AB^* + C \rightarrow ABC \text{ or } AB^* + C \rightarrow AC + B \]

(b) reactions of products of the secondary processes (2) to (5) and (6a) with other molecules:

Reactions of radicals or free atoms deserve special consideration. These materials are of themselves rich in energy and very reactive, and hence can react in turn. If these reactions again produce reactive structures, the process repeats itself. Accordingly, as soon as an activated molecule has reacted, a considerable number of molecules take part in subsequent reactions. This constitutes a chain reaction. Instances are known in which these chains have 100 to 1000 links or more. A chain reaction is broken if the union of atoms or radicals is accompanied by loss of their energy.

These secondary processes proceed as sequels to the primary process, which initiated them. They occur either alone, or concurrently to different extents. Consequently, they determine the variety of the chemical effects of light and also the respective quantum yields. Obviously, there will be a strict equivalence between the absorbed light quanta and the reacting molecules in those cases in which a single chemical reaction follows the primary process. If energy is lost through physical secondary processes—particularly (1)—and likewise in cases in which products of a photo-dissociation reunite to regenerate the initial product, quantum yields less than unity may be expected. On the other hand, if chain reactions are started by the formation of free radicals or atoms, the quantum yields may be greater than unity, even though partial loss of energy occurs because of concurrent secondary processes of other kinds.

A fundamental condition for the entrance of active molecules into chemically significant secondary processes is that no such reaction is possible if its initiation requires more energy than corresponds to the energy content of the activated molecule. Consequently, chemical reactions depend on various factors, such as the nature of the particular system, the accompanying materials, the form of aggregation, etc. Especially important is the fact that a light-activated molecule retains its excess energy for a limited time only (10^{-8} seconds). At the expiration of this period, energy is evolved again, for the most part as heat. Consequently, a chemical reaction cannot be detected at all, unless it is possible for the activated molecule (during its life period) to come in contact with other species of reactive molecules. It is therefore illuminating that the concentration of such acceptors is a determining factor for the quantum yields.

The formation and life period of activated molecules also play a part in light-sensitive systems that are in equilibrium. The equilibrium may be shifted because one of the partners absorbs light and is thus activated. Such photochemical equilibria differ from true equilibria by the fact that their maintenance demands a continuous supply of light. Therefore it is better to use the term stationary state. Frequently, a photoreaction can be detected by the fact that in the stationary state, a member of the photo-equilibrium can be easily recognized, whereas in the normal equilibrium (dark reaction) its quantity is too small to be revealed by the same test.

The effect of temperature on photoreactions is ordinarily quite small. This is in contrast to the influence of this factor on many purely chemical changes, where it is often considerable. Consequently, most photo-reactions can be observed at room temperature. The difference in the temperature effect is understandable if it is noted that one light quantum represents a quantity of energy that is quite considerable when calculated in calories. This is particularly true when the irradiation is by means of light of high frequency, i.e., of short wave length. For instance, one quantum of ultraviolet (wave length 2000 A. U.) corresponds to 142 calories per mole. In contrast to these high figures, the relatively small energy supplied by warming a system to the boiling point plays no significant role.

An acquaintance with the foregoing fundamentals is indispensable to an understanding of the chemical action of light. Many photoreactions proceed to such extents that they can easily be detected and demonstrated. Spot reactions often serve this purpose admirably.

34. Photochemical Decomposition (Photolysis) of Metal Oxalates. Certain oxalates decompose if they are exposed to daylight or irradiated with ultraviolet light. All such cases involve metals that can form oxalates at different valences. The photodecomposition always proceeds with loss of CO2 by the oxalate.
at the higher valence, which is thus converted into the oxalate of the lower valence. Since the decrease in valence is a reduction, and the conversion of the oxalate radical \((\text{C}_2\text{O}_4)^{2-}\) into \(\text{CO}_2\) is an oxidation, this photolysis of oxalates is an inner-molecular or isomolecular redox reaction.\(^2\)

Examples of the photochemical redox reactions of oxalates are:

\[
\text{Fe}_2\left(\text{C}_2\text{O}_4\right)_3 \rightarrow 2\text{FeC}_2\text{O}_4 + 2\text{CO}_2 \\
\text{UO}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow \text{U(C}_2\text{O}_4)_2 + 2\text{H}_2\text{O} + 2\text{CO}_2 \\
2\text{Ce}(\text{C}_2\text{O}_4)_3 \rightarrow \text{Ce}_2(\text{C}_2\text{O}_4)_3 + 2\text{CO}_2
\]

The decomposition of Eder's solution is a further instance of the photolysis of oxalates. It contains ammonium oxalate and mercuric chloride. When exposed to light, mercurous chloride separates:

\[
2\text{HgCl}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{HgCl}_2 + 2\text{CO}_2 + 2\text{NH}_4\text{Cl}
\]

The decomposition is proportional to the intensity of the light, and this effect was formerly used to measure light intensities. In view of the photolysis of metal oxalates, as discussed in the foregoing, it is likely that the mercuric oxalate, or the complex oxalates, in Eder's solution forms mercurous oxalate, and this then combines with chloride ions to form mercurous chloride.

It is noteworthy that the precipitation of mercurous chloride from Eder's solution in visible light is accelerated strongly by traces of iron salts and of certain fluorescent dyes. Probably the discovery by Eder in 1880 of the light sensitivity of a \(\text{HgCl}_2 - (\text{NH}_4)_2\text{C}_2\text{O}_4\) solution was due to the fact that the chemicals used at that time were not free of iron. The action of iron salts involves a catalysis reaction (cf. experiment 47). In contrast, the action of dyes is a typical photosensitization. The addition of uranyl salts also increases the light sensitivity of Eder's solution.

Procedure: (a) Photolysis of ferric oxalate. Mixtures made from 1 drop of 1 \(N\) ferric chloride and 1 drop of \(1 N\) oxalic acid are placed in adjacent depressions of a white spot plate. One mixture is covered with a metal shield to protect it from the action of light. The plate is then exposed to strong sunlight or placed under a quartz lamp for 10 to 15 minutes. Two or three drops of concentrated phosphoric acid are added (cf. experiment 35) and two drops of 2 per cent \(\alpha, \alpha'\text{-dipyridyl}\) solution in 1 \(N\) HCl. A pink to red color appears in the exposed specimen (ferrous \(\alpha, \alpha'\text{-dipyridyl salt}\)), whereas the unilluminated mixture remains colorless.

(b) Photolysis of uranyl oxalate. Freshly precipitated uranyl hydroxide is dissolved in 1 \(N\) oxalic acid and 2 or 3 ml. of this solution are placed in the bulb of the gas evolution apparatus [see Part III, J. CHEM. EDUC., 20, 243 (1943)]. A drop of 0.01 \(N\) sodium carbonate solution, reddened with phenolphthalein, is placed on the base of the stopper. The closed apparatus is then subjected to the action of sunlight. Within a few minutes, the color of the carbonate solution is discharged, due to the action of \(\text{CO}_2\) produced. (c) Photolysis of ceric oxalate. Mixtures prepared from two drops of 2 per cent ceric sulfate solution and two drops of \(1 N\) oxalic acid are placed in adjacent depressions of a spot plate. One mixture is shielded with a metal plate. After exposure to strong sunlight or ultraviolet light for about three minutes, the irradiated mixture shows a white precipitate (cerous oxalate), while the precipitate in the protected mixture remains yellow-brown. (d) Photolysis of Eder's solution is accomplished with and without activators. Mixtures prepared from two drops of 4 per cent ammonium oxalate solution and one drop of 5 per cent mercuric chloride solution are placed in adjacent depressions of a black spot plate. One of the mixtures is shielded with a metal plate. The irradiation in strong sunlight is continued until the precipitate of mercurous chloride is barely visible. The covered specimen remains unchanged. The time is noted and both portions of Eder's solution are then protected with a metal plate. The experiment is repeated, but one drop of 0.02 \(N\) ferric chloride solution, or 0.05 per cent uranyl acetate solution, or 0.02 per cent eosin solution, is added to the freshly prepared Eder's solution. The specimens containing the activators are illuminated just as long as was the pure Eder's solution in the previous experiment. In all cases, a much heavier precipitation of mercurous chloride results than in the pure Eder's solution. Consequently, the metal or dye has strongly activated the light sensitivity of Eder's solution.

35. Photochemical Equilibrium in Solutions of Ferric Salts. Aqueous solutions of ferric chloride are stable in the dark; no significant, reversible decomposition occurs: \(\text{FeCl}_3 \rightleftharpoons \text{FeCl}_2 + \text{Cl}^-\). However, on illumination, this decomposition takes place to a detectable extent. Therefore, a new photochemical equilibrium, or the production of a stationary state in which the concentration of ferrous chloride is greater than in the dark, is indicated. This can be demonstrated if the ferrous ion formed by the action of light is immobilized and thus removed from the photo-equilibrium. Consequently, continued illumination, because of the re-establishment of the photo-equilibrium, will again produce ferrous ions that can, in turn, be masked. Ferrous ions can be sequestered by adding \(\alpha, \alpha'\text{-dipyridyl}\), which combines with them to form stable, complex red Fe \((\alpha, \alpha'\text{-dip})_2^{++}\) ions. If, therefore, \(\alpha, \alpha'\text{-dipyridyl solution is added to a ferric chloride solution which is then illuminated, the original bright yellow color gradually changes through pink to red, corresponding to the formation and accumulation of red Fe \((\alpha, \alpha'\text{-dip})_2^{++}\) ions. The mixed solution remains unaltered in the dark, corresponding to the position of the dark equilibrium, in which the concentration of ferrous ions is too low to be detected. Ferric sulfate solutions behave, in this respect, like ferric chloride solutions.

Procedure: Mixtures made from two drops of 1 \(N\) ferric chloride solution and two drops of 2 per cent
pressions of a white spot plate. One mixture is covered with a metal plate and the spot plate exposed to direct sunlight, are placed in adjacent depressions formed. The protected silver chloride will be found unchanged, and also by the reverse reaction (formation of AgCl from its components). Consequently, a complete decomposition of the salt does not occur. Accordingly, the photolysis of finely pulverized silver halides or of precipitated products proceeds more quickly and to a greater extent than with large crystals. The same effect is obtained by adding materials such as sodium nitrite, gelatin, etc., that consume the halogen. The photolysis of AgCl and AgBr in gelatin emulsions, in which the particles are highly dispersed and thus expose a large surface, and also in the presence of sodium nitrite, strictly conforms to the law of equivalence, i.e., the quantum yield is equal to unity. For reasons already discussed, the quantum yield is less than unity in larger crystals or in precipitated products. Silver oxalate also decomposes when illuminated: Ag₂C₂O₄ → 2Ag + 2CO₂. Although this reaction, in contrast to the photolysis of silver halides, is irreversible, silver oxalate is less sensitive to light than the halides.

Procedure: Single drops of 0.5 N HCl are placed next to each other on filter paper. After they have been absorbed, they are spotted with 0.1 N silver nitrate solution. One spot is shielded from the action of the light by a crucible cover. After several seconds, the exposed spot turns violet. The exposure is continued, and after five minutes, the cover is removed. The protected silver chloride will be found unchanged, while the irradiated spot is dark violet.

The effect of halogen-binding materials can be demonstrated as follows: several milliliters of a strong sodium nitrite solution are placed in a crucible (capacity about 30 ml) and acidified with sulfuric acid. The crucible is covered with a filter paper that is spotted first with HCl and then with AgNO₃. A parallel test is set up, but the nitrite is omitted. The discoloration of the exposed silver chloride occurs sooner over the NO₂ vapors, and after equal periods the intensity of the color is also deeper.

39. Acceleration of the Oxidizing Action of Chronic Acid and Chromates by Illumination (Photo-oxidation). At room temperature, chronic acid only slowly attacks certain organic compounds such as sugar, starch, cellulose, etc. Carbon dioxide is produced by this oxidative degradation of the organic compound, and consequently, Cr (VI) is reduced to Cr (III). Alkali bi-
chromates behave analogously. The oxidative action of chromic acid and bichromates is hastened and intensified by illumination. This is the basis of the use of chromic acid in etching and intaglio printing.

Oxygen is furnished by chromic acid:

\[ 2\text{H}_2\text{CrO}_4 \rightarrow \text{Cr}_2\text{O}_7 + 2\text{H}_2\text{O} + 3\text{O}_2 \]
\[ 4\text{H}^+ + 2\text{CrO}_4^{2-} \rightarrow \text{Cr}_2\text{O}_7 + 2\text{H}_2\text{O} + 3\text{O}_2 \]

Consequently, \( \text{H}^+ \) ions disappear in all oxidations by chromic acid. Suitable indicator papers can be used to show the slow oxidation action of chromic acid in the dark and the rapid action in the light, as the \( \text{H}^+ \) ions disappear at different rates.

Brown insoluble chromic chromate, \( \text{Cr}_2(\text{CrO}_4)_3 \), is produced when bichromate solution acts on organic materials such as the cellulose of paper. Since the formation of this highly colored material is more rapid in the light, the photo-oxidation by means of bichromate can be seen easily as a spot reaction on paper.

**Procedure:** Single drops of 0.2 per cent chromic acid solution are placed on two strips of Congo Red paper. Blue spots result. One strip is kept in the dark, the other is illuminated. After several minutes, the blue spot disappears from the exposed paper, and the original red is restored. The spot remains blue on the unilluminated paper.

Single drops of 10 per cent potassium bichromate solution are placed near each other on thick filter paper (S & S 601). After they have soaked in, one spot is covered with a metal plate and the paper is exposed for about 10 minutes. The illuminated spot turns brown. The paper is then plunged into water. The unilluminated yellow spot washes away almost entirely, while the illuminated brown one remains.

40. **Sensitization of the Autoxidation of Ferrous Sulfate by Eosin.** Solutions of ferrous sulfate slowly undergo autoxidation if they stand in contact with the air:

\[ 2\text{FeSO}_4 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Fe(OH)SO}_4 \]
\[ 3\text{Fe(OH)SO}_4 \rightarrow \text{Fe(OH)}_3 + \text{Fe}_2(\text{SO}_4)_3 \]

This autoxidation is accelerated by the presence of eosin, which thus acts as a sensitizer.

**Procedure:** Two drops of freshly prepared 1 per cent ferrous sulfate solution together with two drops of 0.1 per cent eosin solution are placed in each of two adjacent depressions of a white spot plate. One mixture is shielded with a metal cover and the spot plate is placed in direct sunlight. After brief insolation, the exposed mixture becomes turbid, due to the deposition of \( \text{Fe(OH)}_3 \) or basic ferric sulfate. The quantity of precipitate increases as the exposure is lengthened. A precipitate appears in the nonilluminated mixture only after a much longer interval.

41. **The Action of Light on the System Silver Nitrate-Zinc Oxide.** The action of zinc oxide on solutions of silver nitrate under the influence of light is an example both of a photochemical process in a heterogeneous system and also of a photosensitization. At room temperature, and in the dark, zinc oxide has no particular action on silver nitrate. On the other hand, in the light, a considerable deposition of free silver is obtained in a few seconds:

\[ 2\text{AgNO}_3 + \text{ZnO} \rightarrow 2\text{Ag} + \text{Zn}(\text{NO}_3)_2 + \frac{1}{2}\text{O}_2 \]

Consequently, under illumination, zinc oxide exerts a sort of sensitizing action, since pure silver nitrate solutions deposit only small quantities of metallic silver, and then only after long illumination. The chemical basis of this photoreaction probably is that oxygen forms an addition complex with zinc oxide under the action of light. The oxygen is thus activated and forms unstable \( \text{Ag}_x\text{O}_y \) which easily decomposes into its elements. Solutions of mercuric chloride and palladium chloride behave similarly. If illuminated in the presence of zinc oxide, they react:

\[ 2\text{HgCl}_2 + \text{ZnO} \rightarrow \text{Hg}_2\text{Cl}_4 + \text{ZnCl}_2 + \frac{1}{2}\text{O}_2 \]
\[ \text{FeCl}_3 + \text{ZnO} \rightarrow \text{FeCl}_2 + \text{ZnCl}_2 + \frac{1}{2}\text{O}_2 \]

The mechanism of these reactions is probably analogous to that of silver nitrate.

**Procedure:** Two adjacent depressions of a spot plate are charged with several milligrams (tip of knife blade) of finely powered zinc oxide. Three drops of 0.1 N silver nitrate solution are added to each. One suspension is immediately covered with a metal shield. When placed in direct sunlight, the insolated specimen turns quite black within one minute, while the other remains unchanged.

42. **Photochemical Autoxidation of Iodoform.** Solid iodoform is not decomposed when irradiated. If, however, its solution in benzene, ether, carbon disulfide, etc., is exposed to sunlight, iodine is quickly liberated and produces a violet or brown solution. The liberation of iodine is the result of an autoxidation, \( \frac{1}{5} \) coming from the reaction (1) and \( \frac{1}{5} \) from reaction (2),

\[ 2\text{CH}_3\text{I} + 5\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 3\text{I}_2 \]  \( \text{(1)} \)
\[ 2\text{CH}_3\text{I} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 3\text{I}_2 \]  \( \text{(2)} \)

Probably the activated \( \text{CH}_3\text{I}^\ast \) molecules produced by irradiation decompose into radicals which in turn react with the oxygen of the air. This view is supported by the fact that a solution of iodoform, in which the liberation of iodine is started by a brief illumination, continues to react when placed in the dark.

**Procedure:** Two drops of 0.1 per cent solution of iodoform in benzene are placed in adjacent depressions of a spot plate. One is shielded. When exposed to sunlight, the unprotected solution turns brown within a few seconds and the color constantly deepens. After about one minute, the illuminated solution is dark brown, whereas the other has changed scarcely at all.

43. **Activation by Light of the Addition of Bromine to Benzene.** Benzene, an unsaturated compound, takes up free bromine; the removal of each double

\[ \text{C}_{6}\text{H}_{5}\text{I} \]
bond of the benzene ring involves one molecule of bromine. The formation of hexabromobenzene, C₆H₅Br₆, is favored by light, probably by activation of bromine molecules, which then dissociate into atoms. It should be noted that the analogous formation of chlorobenzene from benzene and chlorine has an enormously high quantum yield (10⁹).

**Procedure:** A drop of bromine is placed in 5 ml. of benzene. Three drops of this solution are placed in each of two adjacent depressions of a spot plate. One is covered with a metal shield, and the plate is then illuminated. After the bromine color of the exposed specimen has disappeared, it will be found that the shielded solution has retained its original yellow.

**44. Conversion of λ Sulfur into μ Sulfur in the Light.** Crystalline sulfur (S λ) is quite soluble in carbon disulfide and other nitrogen-free organic liquids. Amorphous sulfur (S μ), in contrast, is not soluble in these liquids. It is assumed that the molecule of μ sulfur consists of longer chains of sulfur atoms than does the molecule of λ sulfur. A reversible equilibrium S λ ↔ S μ exists between these modifications. μ sulfur is thermally unstable and can be transformed into λ sulfur by heating.

If solutions of λ sulfur in carbon disulfide, carbon tetrachloride, or benzene are irradiated, this equilibrium is shifted in the direction of the production of more μ sulfur. Accordingly, the solution becomes turbid because of the precipitation of insoluble μ sulfur. The opposing reaction proceeds in the dark. These changes are an instance of photo-equilibrium, and also an example of a polymerization brought about by light.

**Procedure:** Five drops of a saturated carbon tetrachloride solution of sulfur are placed in each of two adjacent depressions of a black spot plate. One portion is covered with a metal plate. After about 10 minutes' exposure under an ultraviolet lamp, a turbidity appears, and increases as the irradiation continues. No precipitate is obtained in the shielded solution, even after 30 minutes. The carbon tetrachloride lost during the irradiation should be replaced from time to time.

**45. Acceleration by Light of a Reaction of Aromatic Nitroso Compounds.** A water solution of sodium pentacyano ammino ferroate, Na₃Fe(CN)₅NH₃, reacts with aromatic nitroso compounds:

\[
\text{Na₃Fe(CN)₅NH₃} + \text{RNO} \rightarrow \text{Na₃Fe(CN)₅RNO} + \text{NH₃}
\]

Consequently, the coordinately bound NH₃ molecule is displaced by a molecule of the nitroso compound. This exchange reaction is accompanied by a color change from bright yellow to violet or green. It can be used for the detection of aromatic nitroso compounds. The reaction is very light sensitive; the rate in the dark is immeasurably slow, but in the light it proceeds very rapidly.

**Procedure:** Mixtures made from three drops of 1 per cent sodium pentacyano ammino ferroate solution and one drop of saturated aqueous or a dilute alcohol solution of α-nitroso-β-naphthol solution are placed in adjacent depressions of a spot plate. One mixture is covered with a metal shield and the spot plate is placed in direct sunlight. The exposed specimen rapidly turns green; the color becomes progressively darker while the unilluminated mixture remains practically unchanged. The gradual change to green is distinctly visible even when the mixture is exposed to diffused light.

**46. Molecular Rearrangement of o-Nitrobenzaldehyde by Light.** When illuminated with ultraviolet light, o-nitrobenzaldehyde (I) rearranges to give o-nitrosobenzoic acid (II):

\[
\text{(I)} \quad \text{CHO} + \text{NO}_2 \rightarrow \text{COOH} - \text{NO}
\]

This rearrangement is an instance both of the production of an isomer by light and of an irreversible inner molecular redox reaction. The conversion of the aldehyde group (CHO) into a carboxyl group (COOH) is an oxidation, and the conversion of the NO₂ group into an NO group constitutes a reduction.

The photochemical transformation occurs with solid nitrobenzaldehyde, and also when it is dissolved in organic liquids. The quantum yield, in all cases, and no matter what the solvent, is exactly 0.5.

The production of o-nitrosobenzoic acid is detected easily by the action of sodium pentacyano ammino ferroate on the irradiated product (see experiment 45). A violet solution is obtained when the NH₃ group of the reagent is replaced by a molecule of the nitroso compound. Since the conversion of the nitro compound into the nitroso compound and the reaction of the latter with the reagent are both photoreactions, this experiment presents the interesting case of the combination of two photoreactions.

**Procedure:** Three drops of 0.5 per cent solution of o-nitrobenzaldehyde in alcohol are placed in each of two nonadjacent depressions of a white spot plate. A drop of 1 per cent water solution of sodium pentacyano ammino ferroate is added to each. One mixture is covered with a metal plate. The exposed mixture, which is yellow because of the reagent, quickly turns violet under the ultraviolet lamp. The protected solution retains its original color, even after five minutes' irradiation.

**47. Catalyzed Reactions Brought About by Photolysis of Ferric Oxalate.** Ferric oxalate, as shown in (1), decomposes into ferrous oxalate and CO₂ on exposure to light. If this photolysis [equations (1) and (2)] proceeds in the presence of a compound M, that can be reduced (Continued on page 506)

**References:**

8 **Wigand, Z. phys. Chemie, 77, 423 (1911).**

9 **Baudisch, Ber., 54, 413 (1921).**


9 **Clichian and Silver, Ber., 34, 2040 (1901).**
by ferrous oxalate, then (in the presence of free oxalic acid) ferric oxalate is regenerated (3). The latter again decomposes, producing ferrous oxalate which reduces M, and so on. Summation of the equations representing this series of reactions gives the net equation (4). This expresses the reduction of M by oxalic acid in light, but does not reveal the participation of ferric oxalate:

\[
\begin{align*}
\text{Ferric oxalate} + h\nu &\rightarrow \text{ferric oxalate}^* \quad (1) \\
\text{Ferric oxalate}^* &\rightarrow \text{ferrous oxalate} + \text{CO}_2 \quad (2) \\
\text{Ferrous oxalate} + M + \text{oxalic acid} &\rightarrow \text{ferric oxalate} + M \text{ (reduced)} \quad (3) \\
M + \text{oxalic acid} + h\nu &\rightarrow \text{CO}_2 + M \text{ (reduced)} \quad (4)
\end{align*}
\]

This series of reactions is a typical example of an intermediate reaction catalysis. In its general form, it states that every slow reducing action of oxalic acid will be catalytically accelerated by addition of ferric salts and then irradiating. In fact, it can be shown that the slow reduction by oxalic acid, of selenious acid, iodine, palladium chloride, tungstic acid, and methylene blue, are hastened by adding a little ferric salt and irradiating.

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