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THE PHOTOCHEMICAL OXIDATION OF FORMIC ACID WITH FERRIC SULPHATE

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by

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INTRODUCTION

In his everyday laboratory practice, the chemist almost constantly employs certain forms of energy such as heat, electricity, mechanical energy, and light to bring about the combination of atoms or the disruption of molecules. In recent years, the latter agency, through photochemical studies, has gained considerable prominence.

Though much more attention has been focused recently on the action of light in bringing about chemical transformation, it should not be overlooked that even the very earliest scientists were not wholly unconscious of its potentialities. As early as 350 B.C., Aristotle noted the influence of light on the formation of the green color of plants, and the converse bleaching in darkness. Vitruvius, 100 B.C., remarked on the bleaching of pigments by light. Writings of the alchemists are full of references to the action of light, but couched in such vague and mystic terms that it is uncertain whether the connotation is abstract or concrete. However, really empirical study did not begin until at the end of the 17th century.

Ray (1670), the botanist, distinguished the action of light from that of air on plant growth. The Prussian Chancellor Bestuchy, the discoverer of "iron tincture", a solution of ferric chloride in alcohol, noticed that the color was discharged in sunlight but recovered to some

extent in darkness. Hence, he may be credited with the discovery of the reversibility of photochemical reactions.

In 1727, Scheele described a large number of photochemical reactions, especially the blackening of silver chloride in sunlight and the subsequent separation of chlorine. He was the first to use the spectrum photochemically, remarking that "horn-silver" (fused silver chloride) became black most readily in the violet rays. It is interesting to note that he attempted to explain this fact in terms of the then prevailing Phlogiston Theory, the violet rays being characterized by a greater readiness to part with phlogiston.

Light sensitiveness of a variety of salts of metals, notably that of mercuric chloride and ammonium oxalate, was observed by Planche, and that of manganese salts by Brandenburg.

Berthollet in 1785 noted the decomposition of water by chlorine in sunlight. This discovery led, about 1886, to the construction of the first chemical photometer or actinometer by Sanssure.

Gay Lussac and Thenard (1809-1810) discovered the influence of light on mixtures of chlorine and hydrogen and chlorine and methane. They considered that light acted similarly to heat, but Davy opposed this idea, citing the great chemical activity of the violet and ultraviolet rays where the heating effect is small. In 1812, Davy discovered

the photochemical synthesis of phosgene gas from carbon monoxide and chlorine.

From this time onwards, increasing numbers of photochemical reactions were recorded. Chevreul, in 1837, published an important work on vegetable colours in which the influence of air and moisture in assisting bleaching was emphasized. An important period begins with the researchers of N de Niepce and Daguerre (1814-1830), which, as is well known, resulted in the first photographic process and gave the needed impetus to this branch of photochemistry.

It is interesting to recall that in all of the early photochemical observations and researches, the only available source of radiation was sunlight. Even until comparatively recent times, scientists have experimented with various reactions using sunlight as the only source of ultraviolet radiations. In all cases, however, the task has been exceedingly slow and tedious, some researches requiring as many as two hundred days exposure.

In recent years, two promising developments have pointed the way to further investigations. One of these is the quartz-mercury lamp (1901), giving rise to a ready means of production of ultraviolet rays for experimental purposes, and the other is the use of fluorescent bodies which are capable of absorbing light of one wave length and giving it out as light of a different wave length.

Before considering in a more detailed way the many

applications and effects of ultraviolet rays, it may be helpful to review briefly the nature of the radiations involved.

It is known that only a portion of all the rays given off by the sun and capable of passing through our atmosphere are chemically active, that is, the ultraviolet rays. These rays are of very short wave length. Every light radiation embodies and may be decomposed into a certain number of periodic disturbances, each of which is the simple element of every radiation. The usual manner of describing undulatory disturbances, such as light, sound, heat, etc., is by the wave length, which depends on the number of vibrations made by the wave per second and the velocity with which the wave travels.

For the purpose of transmitting as much of the ultraviolet portion as possible, quartz lamps have replaced those of glass, which absorbed a very large proportion of the ultraviolet rays. Even the quartz does not transmit ultraviolet rays of a wave length shorter than about 1850 A°. The range of wave length of the rays given off and transmitted by the quartz mercury lamp is noted in the diagram of Figure I; the rays having wave lengths between 3900 A° and 1868 A° are the ultraviolet rays which are invisible to the eye.

When light falls upon a substance, a portion of the incident radiation is reflected, a portion is absorbed,

and a portion is transmitted. It has been shown that only that portion of the incident radiation which is absorbed is effective in producing chemical change. Grotthuss published in 1817 a paper which contained a clear outline of this law. As formulated by him, the law states that only light which is absorbed can produce chemical change. Draper in 1839, studying the hydrogen-chlorine reaction, rediscovered this law and since then it has gone under the name of the Grotthuss-Draper law.

Now according to the electromagnetic theory of light, the emission of light waves from a material source is due to the vibration of minute charged particles, called radiators. These radiators, which may be either atoms or electrons, give rise to electromagnetic waves of the same period as their own, that is, to light waves of a definite length. The advent of the Bohr theory of the atom and the quantum theory of light have aided us materially in obtaining a more distinct mental picture of the phenomena of radiation and absorption of light. Thus, when the mercury in the quartz mercury lamp is excited by means of a current of electricity, in reality energy is being added to the system, the energy content or level of the mercury atom has been increased. In consequence of this added energy, the electrons of the mercury atoms are removed to more remote orbits. Then, as the electrons fall or return to orbits nearer to the nucleus, they do so only by giving up some

of their energy, and this energy is transmitted or dissipated in another form - that of light.

Now if this light striking an atom or molecule of substance subjected to irradiation has the same frequency as that of the atom or molecule, it is absorbed, and as a consequence, the energy level of the atom or molecule is raised. Any one of several things might happen as a result of this increased energy content:

(a) If the energy content is increased to a sufficiently high magnitude, electrons might actually be emitted from the atom. This phenomenon is known as the "photoelectric effect".

(b) Many substances have the ability to absorb light of one wave length and to immediately give it off again either as light of the same or <u>different</u> wave length. In other words, the removal of electrons to outer orbits and the subsequent return to inner orbits, or, we may say, the increase of the inter-atomic or inter-molecular energy level and subsequent return to that of the lower and original level, is not only a continuous process but almost simultaneous. The production of such light in such instances where transmission ceases the instant that the source of irradiation is removed, is spoken of as the phenomenon of Fluorescence.

(c) A great many substances known as "phosphors" have the ability not only to transmit such radiation, but

also to store the absorbed energy and give off light for some time even after the source of irradiation has been removed. In other words, the return of the electrons to inner orbits and the consequent transmission of the stored energy as light, occurs much more slowly than in the case of the substances described in (b). This phenomenon is spoken of as "phosphorescence".

(d) Still another type of result might occur as a consequence of the increased inter-molecular energy. Either chemical decomposition of the substance itself or interaction might take place; again in the presence of a suitable depolarizer, a chemical reaction between the latter and the substance may come about. Thus, with an increase in the energy content of the system comes an increase in its chemical activity. It must be remembered, however, that many photochemical reactions are masked or complicated by secondary reactions.

When the absorbing system is polyatomic, the energy absorbed is not necessarily wholly associated with an electronic change, but may also be distributed between vibrational and rotational degrees of freedom of the absorbant.

The quantum theory of photochemical processes, therefore, accounts for the existence of photochemical reactions by the presence in the system of an energy-rich species and also of species with which such energy-rich

atoms or molecules may react. The nature of the chemical change brought about by the agency of the light will depend on the normal chemical reactivity of the system and on the available energy. It is thus possible for all such chemical reactions as occur in the dark, to occur with one of the constituents activated by light. It is, however, possible that reactions may occur in the light, which occur only to a negligible extent in the dark, by reason of the larger units of activating energy involved.

It is interesting to note that whereas chemists at one time believed only the ultraviolet portion of the spectrum to be capable of instigating chemical change in substances, they have gradually come to accept a broader viewpoint. We have reason to believe that the extreme-ultraviolet rays are perhaps even more effective in bringing about chemical change than the near ultraviolet. We know that the infra-red portion of the spectrum is capable of bringing about chemical change and also that it is possible to ionize certain elementary gases, even unto the inert members, by means of X-ray irradiation. Physicists have found that under such irradiation, some of these inert gases apparently form polyatomic molecules. Thus, it seems quite likely that if such a process is a supplying of the irradiated body with sufficient energy by light of frequency corresponding to that of the substance in question, we should perhaps be able to bring about certain chemical

changes by means of electrical or even magnetic waves.

As mentioned and used above, the application of the Bohr concept of atomic structure and the quantum theory seem to afford us the best explanation of the general mechanism of photochemical change; however, even this is not entirely free of limitations. Thus, H. S. Taylor[1] states: "The modern theory of absorption and emission of radiation by quanta is at once both an amplification and limitation of the fundamental law of photochemistry formulated by Grotthuss and later restated by Draper.....In so far as the quantum theory of absorption sets a limit to the energy available in a single absorption act, it also sets a limit to the nature of chemical change that can result from such absorption. Thus, for example, if the absorbing system be composed of a single type of diatomic molecules and the light energy absorbed per quantum is less than the energy of dissociation of such molecules, it follows that such dissociation cannot occur as the result of absorption of a single quantum."

HISTORICAL

A. General Historical

Photochemistry has become so vast that it must, in reality, be treated as a separate branch of chemistry. Like every other branch of science, it has grown from a few of its early scattered and rather unscientific observations, as briefly noted in the Introduction, to studies of hundreds of photochemical reactions, the majority of which have been, with very few exceptions, purely qualitative without any attempt at stoichiometrical studies. Then followed attempts to obtain more fundamental information with regard to the actual mechanism of the photochemical process involved. In the opinion of Plotnikow[2], we are at present in this latter stage of development, involving a study of the fundamentals, from which it is hoped that basic theories of the photochemical mechanism will be found, and which will give us a more satisfactory and thorough understanding of photochemistry.

A study of the literature on photochemistry shows that the subject is in a very chaotic and unsatisfactory state. The many contradictions found are, without question, a result of not only a diversity of experimental conditions, especially with regard to the source and the kind of irradiation, but also because these conditions have not been carefully described and defined. Consequently, it has

been impossible, in most cases, for other investigators to corroborate the published observations.

Considerable attention in recent years has been given to the ozone and the hydrogen chloride reactions with a view to a more fundamental study of photochemistry. Even these, at one time supposedly simple reactions, have proven themselves to be much more complicated than ever before conceived, and consequently many points of disagreement have arisen.

Almost equal attention has been devoted to a study of reactions with a view to substantiating or disproving Einstein's law of Photochemical Equivalence, but to date the number of cases in which the law does not apply greatly outnumber those in which it does. However, since the law applies only to the primary processes involved, it is possible that in most cases it is so hard to differentiate between the primary and the secondary photochemical processes that no definite conclusion can be deduced as to the validity of the law.

In view of the great scope of photochemistry and the hundreds of reactions, both inorganic and organic, which have been studied, it is quite obvious that this paper must limit itself to a historical discussion of only those reactions which are pertinent to the problem which we have investigated.

Since the time of Berzelius, it has been generally recognized that many reactions which do not proceed under the usual conditions may be made to progress in the presence of certain substances, denominated catalysts. Likewise, it began to be observed that light had a profound influence on many chemical reactions, and, as mentioned previously, that the radiations of short wave length, comprising the ultraviolet region, are particularly active in this respect. Some of the reactions thus brought about may also be affected with ordinary catalysts, while in other cases it has not yet been found possible to carry on the reaction without access of light. This does not, however, necessarily imply that the action of light can be placed in the same category as that of catalysts.

In drawing attention to the similarity of numerous catalytic and photochemical reactions, Bancroft[3] suggests that in contact catalysis, the formation of definite or indefinite chemical compounds with the solid catalysts is not in itself the essential thing, but is merely the step in the formation of the free radical which is the real reacting substance. Ultraviolet radiation is considered also to aid in the formation of free radicals. The problem on the photochemical side is to determine what radicals are formed and what ultraviolet rays produce them. If, as seems probable, each chemical bond corresponds to one or more absorption lines, it should be possible theoretically

to break or open any desired bond in any given substance by the use of suitable monochromatic light of sufficient intensity under favorable conditions. In other words, there is a possibility of developing an absolutely new technique in organic chemistry.

Various reactions which proceed ordinarily with a catalyst have been studied in its absence by Bourgoin[4], using instead, exposure to the radiation of a quartz mercury lamp. Thus, acetylene was oxidized to acetaldehyde and acetic acid, benzol to phenol, toluol to benzoic acid, and sulphur dioxide to sulphur trioxide. Methyl and ethyl alcohols were also oxidized. Bourgoin fails to mention, on the one hand, whether or not these reactions were purely intra-molecular oxidation-reduction changes, or, on the other hand, whether or not oxygen took part in the reaction. It is quite likely that his experiments were conducted in the presence of atmospheric oxygen.

A number of cases in which radiation (ultraviolet, alpha-ray, X-ray) brings about the same reaction as treatment with ozonized air are considered by Fernau[5]. Thus, sucrose in neutral, acid, or alkaline solution is inverted when subjected to ultraviolet rays. Egg albumin, when exposed to the radiation from radium, is coagulated and ceric hydroxide sols are similarly coagulated. These actions are also brought about when the substances concerned are treated with ozone or hydrogen peroxide.

Reactions which can be induced photochemically and electrochemically have been compared by Smiths and Aten[6]. Either ultraviolet rays transmitted through quartz, or the electrical discharge from an ozonizer, were used to produce photochemical-electrochemical equilibria, leading them to conclude that the action of light and of the electrical discharge is the same, namely, a displacement of the equilibrium in the endothermal direction.

Plotnikow[7] expressed the opinion that every element or compound which has a free valence electron is photochemically unsaturated, that the photoactivity is a periodic function of their atomic numbers, and that every photochemically unsaturated compound is photoactive. Light tends to convert the unsaturated into the saturated, and in the process, energy may be either absorbed or evolved. A photochemically inactive system may be made active by the addition of such substances as uranium, iron, and chlorine which are rich in valence electrons and which, as some maintain, act as catalyzers.

Nazarov[8] regards photochemical effects, at least in their initial stages, as photoelectric effects.

Berthelot and Gaudechon[9] show that photochemical reactions can be divided into two classes, as is also the case with thermochemical reactions, namely (a) exothermic and irreversible, and (b) endothermic and reversible. In both cases, the efficacy of the radiations used increases

with their frequency, which consequently plays the part of potential or of "photochemical temperature". Endothermic changes which are produced thermally only by very high temperatures likewise are produced photochemically only by the extreme ultraviolet rays. Light tends to transform photochemically unsaturated compounds, i.e., those with unbound or weakly bound valence electrons, into photostable ones.

According to Byk, Fehling's solution is decomposed by light of wave lengths less than 400 mμ corresponding with an absorption band in the ultraviolet, whereas the red and yellow waves of the visible absorption bands have no action. The red light absorbed by Fehling's solution is not active enough, unaided, to produce decomposition, whereas in the presence of a suitable reducing agent, its activity might be sufficiently reinforced for it to do so. Thus, Leighton[10] finds that in the presence of quinol within narrow limits of concentration, Fehling's solution is reduced by red light, but is stable in the dark.

B. Photolysis of Organic Compounds

The action of ultraviolet light on organic compounds depends largely on the wave length. Generally speaking, the shorter the wave length, the more fundamental and deep-seated is the decomposition effected. Radiations of long and moderate wave length very often produce polymerization or rearrangement, while compounds of a simple structure are formed from the splitting up of more complex

molecules as the short ultraviolet is approached. The final stage is reached with the production of carbon dioxide, methane, hydrogen, and water. These considerations are made from the viewpoint of irradiation of pure compounds and not in the presence of easily photochemically activated molecules, such as iron or uranium salts.

Reactions facilitated by ultraviolet radiations are not always decompositions. Oxidation and reduction, and likewise various synthetic reactions, are often promoted. In general, light favors endothermic reactions[11]. The decomposition of carbon dioxide into carbon monoxide and oxygen caused at ordinary temperatures by ultraviolet rays, is evidence of the powerful dissociating action of such radiation. This effect is important in the photochemical synthesis of carbohydrates.

Hydrocarbons rayed with ultraviolet generally polymerize; e.g., acetylene yields benzene and a resinous substance. Alcohols, aldehydes, and ketones decompose into carbon monoxide, hydrogen, and hydrocarbons under some conditions. Ethers decompose like alcohols, but yield less hydrogen and more hydrocarbon. Acids may yield carbon dioxide and a hydrocarbon, with some carbon monoxide and hydrogen, probably due to preliminary reduction to aldehyde, but such drastic decomposition does not always take place.

Dibasic acids readily lose carbon dioxide, leaving the monobasic acid. Keto acids react the same in ultra-

violet light as when heated. Esters yield both oxides of carbon, hydrogen, and a hydrocarbon, or they may react similarly to the acids from which they are derived. Sugars react very much as with ferments. Bioses yield monoses; trioses, a monose and a biose, which then yields two monoses. Monoses break up into carbon monoxide, methane, and hydrogen.

Some relation is to be expected between absorption spectrum of a substance and its photochemical activity. According to some authors, the chemical activity depends solely on that part of the absorption spectrum coinciding with the atomic groups affected by photochemical action. The rest of the light energy absorbed appears as heat. This, of course, gives the possibility that photochemical decomposition may differ with different wave lengths, depending on the groups responsible for absorption. Apparently rays of different wave length are absorbed by different groups.

Photochemical oxidation and reduction changes are either equilibria affected by light, or complete decompositions. Photochemical polymerization occurs in many cases. Ketones and aldehydes are especially susceptible to photochemical condensation. Many isomerizations promoted by light are equilibria which can be changed by varying the wave length. In general, rays of long wave length change the labile to the stable form. Ultraviolet rays have the

opposite effect. Photochemical hydrolysis is also very common. Thus, most esters are hydrolyzed by water under the influence of the rays.

Hydrocarbons and their derivatives are very often polymerized by exposure to ultraviolet radiation. Some of those possessing the more complex configurations undergo transformation into stereoisomers. Substituents frequently influence the course of the reaction and are sometimes split off, or take part in secondary reactions. When oxidizing or reducing agents are present, these sometimes enter into the reaction.

Berthelot and Gaudechon[12], 1911, have investigated the action of the ultraviolet rays on a number of typical aromatic compounds. In no case was there observed an evolution of gas or any evidence of decomposition. The addition of uranium salts had no effect. A similar ability to resist decomposition was found in the case of other cyclic compounds (pyrrole, furfural, pyridine) and a few alkaloids. This behavior corresponds with the well known stability of the aromatic nucleus towards heat, light, and chemical reagents. In the case of hexahydrobenzene and piperidine, where the double bonds have disappeared, decomposition took place, the latter compound evolving hydrogen. When the nucleus is attached to a straight chain, that portion of the compound is attacked.

Berthelot[13] found benzene to remain unaltered when exposed to bright sunlight for several months in sealed tubes containing hydrogen or argon, although it combined with oxygen, yielding resinous products, if placed over mercury. A brown sediment, which is derived from thiophene present in the hydrocarbon, forms at the junction of the liquids.

The fact that the most easily isolabile products of the auto-oxidation in light of benzene homologues, are carboxy-acids is attributed by Suida[14] to the relative instability of the intermediate products.

Methyl substituted benzenes undergo auto-oxidation when irradiated, and the action is accelerated by the presence of small quantities of nitrobenzene or of one of the nitrotoluenes. The oxidation of xylene occurs more than twice as rapidly as that of the toluenes, and para-xylene oxidizes more rapidly than the ortho-isomer. The oxidation of 4-nitro-m-xylene under the influence of light resembles that of para-nitrotoluene, but is feebler.

Kailan[15] exposed toluene in the dark for about two years to the action of the radiation from a preparation containing 0.080 grams of radium in a glass envelope one millimeter in thickness, and found that less than 0.25% of the toluene had been changed. The products formed included benzaldehyde, benzoic acid, and apparently formic acid. The increase in the density of the toluene and the weight of

the residue left on evaporation indicate that the principal product of the reaction consists of a yellow, viscous mass, composed presumably of hydrocarbons and condensation products of benzaldehyde. Changes of a similar nature and order of magnitude are produced in toluene when exposed for twenty-two hours to the radiation from a quartz mercury lamp at a distance of eight to nine centimeters.

Ethylene[16] is slowly polymerized by radiation from a quartz mercury lamp of 110 volts, but the action is incomplete even after 134 hours. With a 500 volt lamp, however, polymerization is complete, both for ethylene and acetylene. Ethane and methane are not affected by ultraviolet, but in the presence of oxygen, the former is eventually completely oxidized to carbon dioxide and water.

By the action of ultraviolet rays on a mixture of ethylene and oxygen, formic acid is produced[17]. Acetylene behaves similarly. In general, in the photochemical reactions with ethylenic and acetylenic compounds in the presence of oxygen, the double and triple linkages are ruptured and simple acids formed, while in the presence of ammonia, cyclic compounds are formed. Ethylene, for example, yields first ammino-ethylenes and then ring formation takes place with production of compounds of the pyrrolidine and pyridine types, which may be regarded as the mother substances of alkaloids.

Investigations of Stobbe and Schmitt[18] show that alkyl iodides, either pure or in solution, do not become colored when preserved in the dark for two and one-half months, but in daylight, a coloration is produced in a few hours in all cases. This coloration does not occur if oxygen is absent.

Henri and Ranc[19], by subjecting a 10% aqueous solution of glycerol for six hours to the action of ultraviolet radiation from a 500 volt quartz mercury lamp, have shown that the glycerol molecule is decomposed with the production of formaldehyde and acids as well as other aldehydic substances. The decomposition is considerably increased by the presence of hydrogen peroxide, the activation being proportional to the quantity of peroxide added.

A detailed study of the photolysis of acetaldehyde has been made by Berthelot and Gaudechon[20], who state that ultraviolet rays of long wave length do not convert the aldehyde into acetic acid in the absence of oxygen. Under the influence of medium and extreme rays, oxidation takes place even in the absence of oxygen, a portion of the aldehyde being converted into acetic acid. The amount of acid produced is far greater when the aldehyde is in the form of vapor than when it is liquid. With rays of wave length 2500 A°, polymerization is rapid, both para and meta acetaldehyde being formed. The presence

of water checks polymerization and resinification, but favor acidification, formic acid being produced in this case and in amount almost equal to that of acetic acid. Of three compounds studied, viz.: acetaldehyde, ethyl alcohol, and acetic acid[21], only acetaldehyde is decomposed by sunlight. Wave lengths greater than 3000 A° decompose acetaldehyde to carbon monoxide and methane. The full direct light of a quartz mercury lamp decomposes all three compounds, ethyl alcohol primarily into acetaldehyde and hydrogen[22], but usually some carbon dioxide and ethane are formed by further decomposition of acetaldehyde. The photolysis of acetic acid in the absence of air, produces a gas which contains 44% carbon dioxide, 17% carbon monoxide, and 39% of combustible gases[23].

A. Frank and E. Pollitzer[24] found that saturated aldehydes of the fatty series decompose smoothly under the action of ultraviolet light into carbon monoxide and hydrocarbon. Condensation products are also formed, but definite compounds could not be isolated from the mixture of condensation and polymerization products. Esters could not be detected. Likewise, the amount of acid is not increased if the action is carried out in the absence of water and oxygen. Unsaturated aldehydes and aromatic aldehydes do not decompose with the formation of gaseous products.

Grossman[25] found that ethyl acetoacetate is decomposed by ultraviolet rays, yielding mainly ethyl acetate and acetic acid. Likewise, acetyl-acetone gives acetic acid and acetone.

Boeseken and Coehn[26] studied the photochemical reduction of ketones by anhydrous alcohol, both by direct sunlight and rays from a quartz mercury lamp. Reduction in sealed tubes gave only pinacols, while the alcohol was oxidized to the corresponding aldehyde. The reaction velocity is independent of the concentration of ketone and proportional to the concentration of the alcohol. The rate of pinacol formation depends greatly on the alcohol employed, methyl and ethyl alcohol acting slower than other primary and secondary alcohols. The rate also depends on the ketone employed, benzophenone being reduced more rapidly than other ketones.

Organic compounds[27] containing a carbonyl group show exceptional sensitiveness toward light. Thus, solutions of ketoses, protected from the air, were found to decompose slowly in sunlight. The reaction consists in the elimination of the carbonyl group and the conversion of the ketose into an alcohol containing one carbon atom less in the molecule. The reaction proceeds much more rapidly when the quartz mercury lamp is used as the source of radiation and is accompanied by subsidiary reactions.

Dorée and Dyer[28] exposed some specially scoured and bleached cotton cloth to the rays of a quartz mercury lamp continuously for a period of one week and then tested the exposed cloth in various ways. The conclusion is drawn that ultraviolet rays under the conditions employed, convert cellulose, with complete loss of tensile strength, into oxy-cellulose.

The action of ultraviolet light on many organic acids or their salts leads to decomposition, but in the cases in which there is unsaturation, the polymerization and isomerization characteristic of multiple bonds often results.

The influence of light upon various acids and their salts is interpreted by Jaeger and Berger[29] largely by ionic equations, and from the results it is concluded that each photochemical reaction is specific and very dependent upon conditions obtaining at the moment, so that it is scarcely ever possible to predict its course.

Kailan[30] has found that when dilute (0.5 to 2.0 N) solutions of acetic, oxalic, malonic, succinic, malic, and tartaric acid are exposed in quartz cells to the action of a quartz mercury lamp, slight decomposition takes place. The speed of decomposition of a dibasic acid is increased by the introduction of an alcoholic hydroxyl group into the molecule. The speed of decomposition increases with length of exposure, but does not increase in

proportion to increasing concentration of the acid.

Marc Landau[31] exposed lactic acid to the action of ultraviolet light and found that in addition to the liberation of gases, other changes occur involving the production of ethyl alcohol, pyruvic acid, and traces of an unidentified substance which reduces ammoniacal silver nitrate in the cold.

Baudisch[32] found that when lactic acid, which had been repeatedly purified from its zinc salt, is irradiated with a quartz mercury lamp (250 volts and 3 to 5 amperes) for about forty hours, the distillate after neutralization with calcium carbonate gives decisive acid reactions. He failed to find any traces of alcohol or methane. Solid calcium lactate, on the other hand, gives, upon irradiation, carbon monoxide, methane, ethane, and hydrogen[33].

Euler and Ryd[34] found that lactic acid, in presence of short wave length ultraviolet rays, undergoes a decomposition analogous to a fermentation with evolution of carbon dioxide. The rate of evolution of carbon dioxide is not accelerated by the presence of either ferrous or ferric salts, but the latter are reduced.

Acetic acid and aniline[35], in equimolecular proportions when exposed to ultraviolet light for 24 hours give nearly 100% yield of acetanilide. Propionic and benzoic acids act similarly but give lower yields of propionanilide and benzanilide.

Berthelot and Gaudechon[36] studied the photochemical decomposition of anhydrous oxalic acid and reported that it was decomposed by ultraviolet light of wave length shorter than 3000 A°. Analysis of the products showed 87% carbon dioxide, 9.5% carbon monoxide, and 3.5% hydrogen, together with traces of formic acid. W. A. Noyes and Kouperman[37] found that the rate of the decomposition for short wave lengths is much increased by the presence of water and evidently depends on the amount of water present.

Volmar[38], in working on the photolysis of dibasic acids, concludes that one carboxyl group of oxalic acid yields carbon dioxide under ultraviolet radiation of about 0.3 micron wave length, giving formic acid. This remaining carboxyl group requires radiation as short as 0.21 micron for its decomposition. In malonic, succinic, and glutaric acids, both carboxyl groups decompose under approximately the latter radiation, but not under the former. This is in harmony with the energy calculations, based on the law of photochemical equivalence previously proposed by Volmar[39]. Thus, the farther the two carboxyl groups are separated by connecting carbon atoms, the less is their reciprocal influence; beginning with succinic acid, the mutual influence has practically disappeared.

Visible light of short wave length and ultraviolet rays have long been employed to assist in reactions involving halogenation. With the exception of fluorine, the halogens,

or their compounds, afford many instances where modification takes place under stimulus of such radiation. Chlorination of toluene in light to make benzyl chloride, benzal chloride, and benzo trichloride and by hydrolysis, benzyl alcohol, benzaldehyde, and benzoic acid therefrom is a procedure of long standing, one in fact which has received considerable commercial use. The chlorination of natural gas (chiefly methane), to obtain carbon tetrachloride and chloroform, represents another development.

C. Photochemical Decomposition of Organic Compounds in the Presence of Iron or Uranium Salts

As was mentioned previously, a photochemically inactive system may be made active by the addition of such substances as chlorine, uranium salts, and iron salts which are rich in valence electrons. Many of the earlier investigators believed that these substances acted as catalysts, but it has been quite definitely shown since then, that these so-called catalysts actually enter into the reaction in a stoichiometrical relation. It is true, in the case of ferric salts and under conditions where the reaction mixture is in contact with air, that the iron salts do have a continuous reaction and act as oxygen carriers, but when the same reactions are carried out in the absence of oxygen, the extent of these reactions depends upon the concentration of the ferric salt present.

In many instances where pure organic compounds are decomposed by light, it has been found that uranium or ferric salts may not only increase the velocity of the same decomposition but might entirely change the character of the decomposition itself. A careful study of the nature of photochemical decompositions of organic compounds in the presence of uranium or ferric salts, show that such reactions are more aptly classified as "photochemical oxidations."

Early in the 17th century, the Prussian Chancellor, Bestuchy, noticed that in his "iron tincture", a solution of ferric chloride in alcohol, that the color was discharged in sunlight but recovered to some extent in darkness. This is without doubt the first observation recorded concerning the photochemical action of ferric salts on organic compounds.

J. M. Eder[40] in 1880 and Vries[41] in 1885, studied the action of ordinary light on aqueous solutions of ferric chloride and oxalic acid, tartaric, and citric acids respectively. In each case, it was found that the ferric salt was reduced to the ferrous salt and carbon dioxide was liberated. Since the experiments were carried out in the open air, it was concluded that the ferric salt acted catalytically as a carrier of oxygen.

A. Benrath[42] placed various organic substances in sealed tubes along with ferric chloride and exposed them to sunlight. The experiments were only qualitative

in nature, but were an attempt to show the oxidizing action of the ferric salt under the influence of light. On the basis of qualitative tests, he postulates the following products for each of the substances irradiated:

I. CH_3OH + $FeCl_3$ $\longrightarrow$ CH_3Cl, HCHO, HCl, $FeCl_2$

II. HCHO + $FeCl_3$ $\longrightarrow$ HCOOH, HCl, $FeCl_2$

III. HCOOH + $FeCl_3$ $\longrightarrow$ CO_2, HCl, $FeCl_2$

IV. C_2H_5OH (abs.) + $FeCl_3$ $\longrightarrow$ CH_3CHO, C_2H_5Cl, HCl, $FeCl_2$

V. $C_2H_5OC_2H_5$ + $FeCl_3$ $\longrightarrow$ CH_3CHO, HCl, C_4H_9Cl or C_2H_5Cl, $FeCl_2$

VI. CH_3CHO + $FeCl_3$ $\longrightarrow$ CH_3COOH, HCl, $FeCl_2$

VII. CH_3COOH + $FeCl_3$ $\longrightarrow$ A-rose-red-powder

The action of ultraviolet light on ferric sulphate, nitrate, and chloride was noted by Ross[43] who used an arc between aluminum electrodes as a source of ultraviolet light. The action on ferric salts is much increased by the presence of some organic compound, as cane sugar, which of itself will not reduce these salts but does so under the influence of radiation. The amount of ferric salt reduced is approximately proportional to the time of exposure.

Varying the temperature of any ferric salt solution was found to have only a very slight effect on the rate of reduction. It has been shown that methyl alcoholic ferric chloride is reduced in sunlight, ferrous chloride, hydrogen chloride, and formaldehyde being the primary

products while methyl chloride and formaldehyde compounds are obtained by secondary reactions.

When Benrath[44] exposed aqueous solutions of alpha or beta hydroxy acids to ultraviolet light in the presence of ferrous salts, ketonic acids are first formed and these are then decomposed into carbon dioxide and aldehydes or ketones. It is quite probable, however, that Benrath conducted his experiments in the open, in consequence of which the ferrous salt was oxidized to the ferric salt and the latter was the photochemical oxidizing agent.

Euler and Ryd[45], working with lactic acid in the presence of short ultraviolet rays, found that this compound undergoes decomposition analogous to a fermentation with evolution of carbon dioxide. They state that the rate of the carbon dioxide evolution is not accelerated by the presence of either ferric or ferrous salts, but the former are reduced.

The formation of reducing substances and carbon dioxide when tartaric acid is exposed to ultraviolet radiation was noted by Euler and Ryd[46]. In this case, ferric but not ferrous salts increase the rate of gas evolution and the ferric salt is itself reduced at the same time.

Neuberg[47] compared the chemical changes produced by ultraviolet light from a quartz mercury lamp and sunlight.

He states that catalysts, especially iron salts, bring about marked changes in various substances exposed to sunlight. Dextrose, sucrose, lactic acid, and benzoic acid were examined. Uranium salts were also used as catalysts.

In 1914, Winther and Howe[48] made a study of the photochemical decomposition of iron oxalate, succinate, tartrate, citrate, and acetate with ultraviolet rays. The reaction velocity is approximately constant throughout the whole change. The quantum sensitiveness is greater than unity showing a catalytic light reaction.

Bolin[49] in 1914 conducted a series of experiments on sodium lactate, exposing a solution of the compound and uranium sulphate in the one case and ferric sulphate in the other to the effect of ultraviolet light. His experiments were conducted in the absence of air in all cases. The acetaldehyde which was liberated in the reaction was absorbed in tenth normal sodium bisulphite solution; the excess bisulphite was titrated with iodine solution. The bound bisulphite was then liberated by sodium carbonate, and the freed bisulphite was again titrated with the standard iodine solution. From these results, the amount of acetaldehyde liberated from the initial reaction was calculated. Readings were taken at hourly intervals, and the amount of aldehyde liberated was plotted against time.

Since the curves obtained from the uranium sulphate and ferric sulphate were practically identical,

Bolin concludes that these two compounds act in the same manner. Both the ferric and the uranium salts were reduced. The same experiment conducted at various temperatures showed that variations in temperature have for all purposes a negligible effect. He offered the following equation for the reaction of sodium lactate and ferric sulphate on irradiation with ultraviolet light:

$$CH_3CHOHCOO' + 2\ Fe'''\ + H' \longrightarrow CH_3CHO + CO_2 + 2\ Fe'' + 2H'$$

Volmar[50] in 1923 found that hydroxy acids and their salts undergo photolysis. A one per cent solution of tartaric acid, after three hours exposure, gave 3.5 cc. of gas having the composition: CO_2, 66%; CO, 10%; H_2, 21% and hydrocarbons, 3%. The solution contained aldehydes and small quantities of a reducing substance of the nature of a sugar. The homologues of tartaric acid behave in a similar manner and the decomposition, he states, is accelerated by the presence of catalysts such as uranyl acetate.

In 1927, H. S. Fry and E. G. Gerwe[51] conducted a series of experiments on citric acid in solution with ferric sulphate. In general, the procedure was to expose a solution of the acid and ferric sulphate to the effect of ultraviolet light, absorbing the liberated carbon dioxide in Ascarite. The acid was present in large excess in all instances and the ferric sulphate solution was of known concentration. The results of the experiment showed that

the weight of the carbon dioxide liberated was in direct proportion to the amount of ferric sulphate reduced. From the stoichiometrical ratio, $Fe_2(SO_4)_3 : 3CO_2$, they proposed the following equation for the reaction:

$$(CH_2COOH)_2 : C(OH)COOH + Fe_2(SO_4)_3 \longrightarrow$$

$$CH_3COCH_3 + 2FeSO_4 + H_2SO_4 + 3CO_2.$$

OBJECT OF THIS RESEARCH

In 1928-29 and previous to undertaking the present investigation, the author[52] attempted to make a quantitative study of the photochemical oxidation of lactic acid in aqueous solution containing ferric sulphate. However, in view of the varied decomposition of lactic acid into simpler carbon compounds and the possibility of subsequent photolysis of these, as previously noted, it seemed advisable to make a study of the photochemical oxidation of simpler carbon compounds in order to gain thereby a more complete understanding of the decomposition of the more complex carbon compounds under identical experimental conditions.

It may be again mentioned that, though some of this work has been investigated by others, the literature is markedly lacking in satisfactory quantitative data. Because of this, the varied and inadequately defined experimental conditions, and also the many disagreements between different authors, it seemed advisable to investigate this problem under standardized conditions throughout and under a strictly quantitative procedure. Consequently, it was decided to initiate a study of the photochemical oxidation with ferric sulphate of aqueous solutions of first, formic acid, then formaldehyde, and finally the corresponding methyl alcohol. These carbon compounds are the simplest representatives of an acid, an aldehyde, and

an alcohol, respectively. It is evident that study of the reaction with methyl alcohol would be more complex than that with formaldehyde, and the latter would be more involved than that of formic acid. This is the reason for beginning this proposed extended study with the reaction of formic acid.

Before going on to the discussion of the experimental procedure, it is well to review briefly the more important photochemical work on formic acid as recorded in the literature.

Berthelot and Gaudechon[53], as a result of their work, concluded that formic acid decomposes when subjected to the influence of ultraviolet radiation, in two ways, as represented in the following equations:

$$\text{(A)}\quad HCOOH \xrightarrow{\text{UVL } 2500\text{-}3000\ A^{\circ}} H_2O + CO$$

$$\text{(B)}\quad HCOOH \xrightarrow{\text{extreme ultraviolet}} H_2 + CO_2$$

Allmand and Reeves[54] extended the work of Berthelot and Gaudechon, but upon irradiating aqueous solutions of formic acid, they obtained both reactions (A) and (B) in filtered light as well as in whole light, which is in direct contradiction to the conclusions of Berthelot and Gaudechon. Instead, they found, on analysis of the gaseous products, that the relative extent of these reactions depended largely upon the concentration of the formic acid

solution, and not on the wave length of the absorbed radiation. Thus, the solution of higher concentration (2.4 normal) yielded preponderately CO_2, much HCHO, its condensation and reduction products, and only small amounts of CO and H_2. While in a 0.113 normal solution, the yield of CO and H_2 relative to CO_2 was markedly increased but no HCHO was formed. In the case of this latter solution, they find that reaction (B) occurs about six times more frequently than does (A). From this they conclude that in the case of the 2.4 normal solution, the respective frequencies of reactions (A) and (B) remain the same, but the photolysis of the formic acid in higher concentration is accompanied by secondary reactions. Thus, the deficiency of CO and H_2, present to the extent of only 0.5% of the CO_2, and the presence of HCHO among the decomposition products of the more concentrated formic acid solution, indicate the following secondary reactions: (H_2' and CO' indicate activated molecules)

$$H_2' + HCOOH \longrightarrow HCHO + HOH$$

$$CO' + HCOOH \longrightarrow CO_2 + HCHO.$$

The proof of this is further attested by the deficiency of HCHO and corresponding increase in the amount of H_2 and CO in the case of the more dilute solution.

In the more dilute solution, these activated hydrogen and carbon monoxide molecules lose their energy by collision with water before meeting formic acid molecules,

and therefore, no secondary reactions occur. In the case of the more concentrated solution, Allmand and Reeves do not believe that the H_2' and CO' molecules could mutually destroy one another in view of the fact of the necessity of assuming equal probabilities for the two primary reactions, and these molecules could hardly collide before deactivation in preference to the collision with formic acid molecules.

It is interesting to note that Ramsperger and Porter[55], upon irradiating gaseous HCOOH with the full light of a quartz mercury lamp, obtained the ratio $(CO + H_2O) : (CO_2 + H_2) :: 64 : 36$; while Taylor and Bates[56], using monochromatic light (2536 A°) found a different ratio of 76 : 24. Until we obtain a more complete insight into the mechanism of molecular absorption of energy and the molecular kinetics involved, we can only speculate concerning the cause of these varying relative ratios.

Hatt[57] irradiated uranyl formate and found the uranyl ion to be reduced to uranous ion and this latter shows a retarding effect on the rate of decomposition, which he attributes to the absorption of active light by it. He found that the initial rate of reaction is proportional to the light intensity, which was varied in the ratio of 1 : 280, and estimates the quantum yield to be about 0.4. The decomposition was found to be very sensitive to the addition of salts and acids, all of which cause a decrease of the reaction rate.

EXPERIMENTAL

A. Apparatus

A Victor water-cooled Uviarc quartz mercury lamp, manufactured by the Victor X-Ray Corporation of Chicago, Illinois, was used as the source of ultraviolet radiation. Quartz test tubes contained the reaction mixtures, while a drying train removed the moisture from the liberated gas and ascarite towers were used to absorb the carbon dioxide.

The spectra of the lamp extends from 1850 A° to 14,000 A° and the radiation of wave length less than 14,000 A° is largely concentrated in a close pair of yellow green lines.

In making a series of determinations, it is of the utmost importance to maintain exactly similar conditions and to irradiate each time the same volume and area of solution. To do this, it is absolutely necessary that opportunity be given for equal volumes of reaction mixture to absorb the same amount of radiation per unit of time. Consequently, the surface of both the reaction tubes and the window of the lamp must be free from all dirt and grease, since these cut out much of the radiation and in addition, exactly the same relative positions of the lamp and the reaction tubes must be maintained in all determinations. To make certain of this latter precaution,

FIG I THE QUARTZ-LIGHT SPECTRUM

WAVE-LENGTHS IN ANGSTROM UNITS

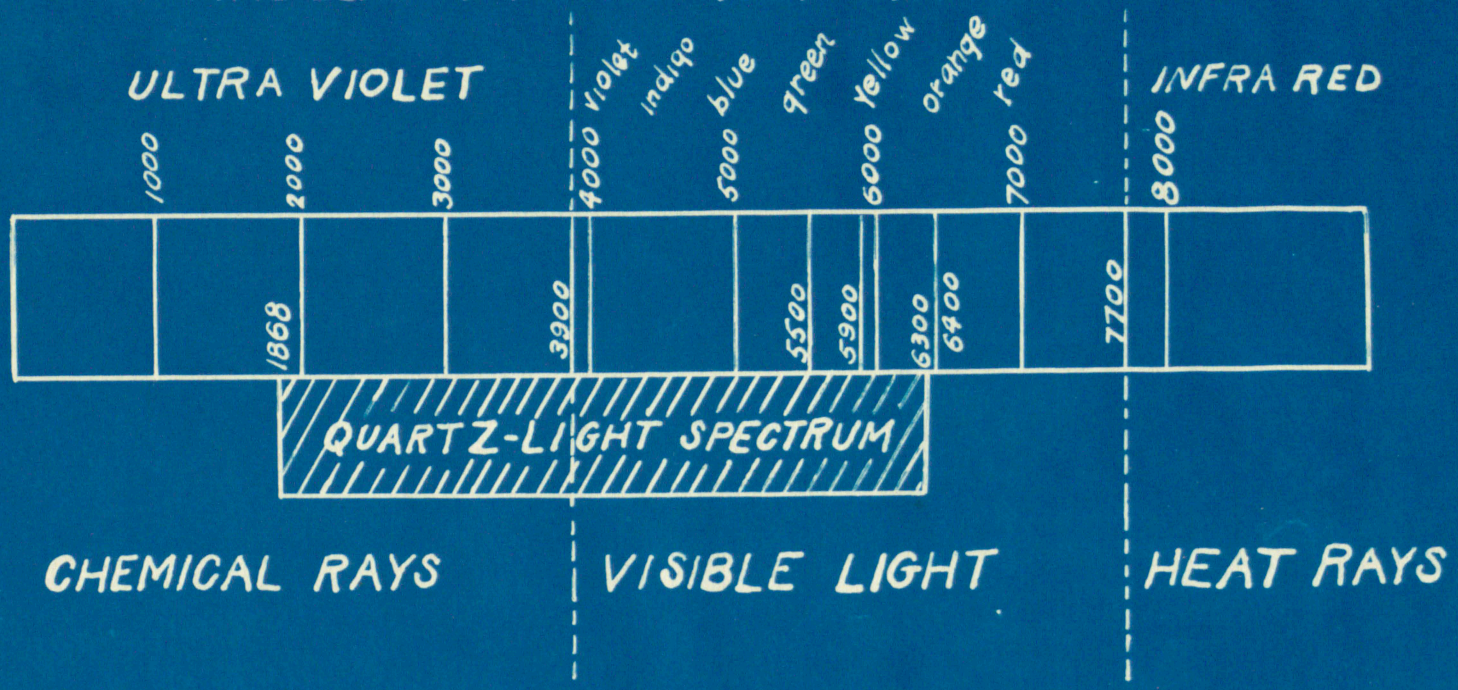
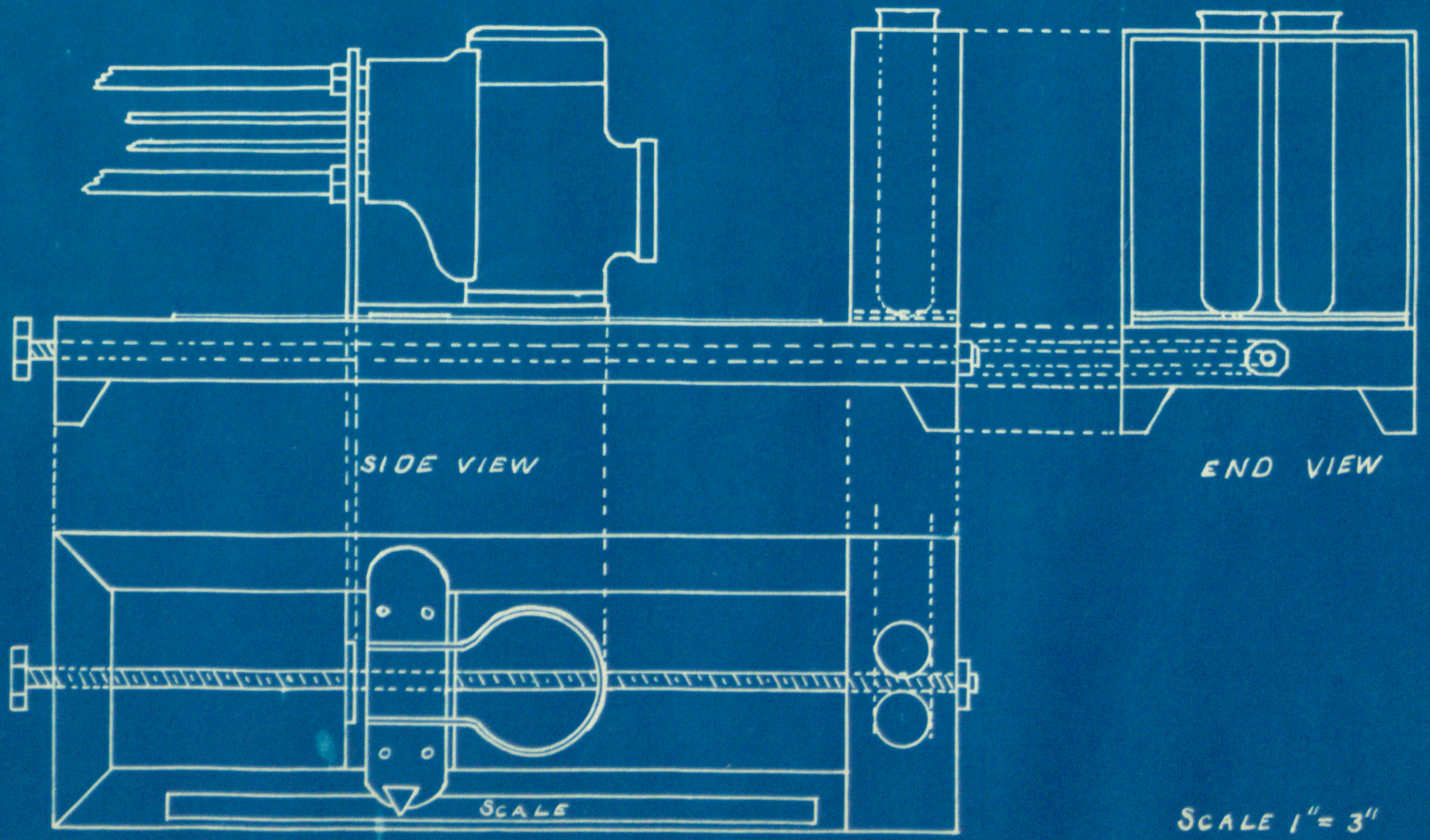


FIG II LAMP AND REACTION TUBE SUPPORT



SCALE 1" = 3"

the apparatus as shown in Figure II was specially designed. The reaction tubes are thereby held in a rigid position so that the central point of the quartz mercury tube is on a level with the perpendicular center of the body of the liquid in each tube irradiated. The tubes are also held in such a position that a line drawn from the exact center of the quartz mercury tube passes exactly between the duplicate reaction tubes. There is a micro-screw adjustment on the apparatus which makes it possible to vary the distance of the lamp from the tubes, while at the same time maintaining the line of center. The scale attachment measures directly the distance in centimeters between the quartz mercury tube and the nearest wall of the reaction tube. This distance in all of the experiments was maintained at 15 centimeters.

The quartz reaction tubes were 2.75 cm. in diameter and 15 cm. in length, having a capacity of about 60 cc. The drying train consisted of a small calcium chloride tube filled with glass wool, followed by two U tubes containing calcium chloride which had previously been saturated with carbon dioxide.

The absorption apparatus consisted of an Ascarite tower, similar to the Stesson-Norton glass-stoppered carbon dioxide absorption unit, filled with Ascarite. The reaction tube, drying train, and absorption unit were set up in duplicate.

B. Preliminary Experiments

In order that a quantitative procedure could be outlined, a number of preliminary experiments were planned and conducted as follows.

First of all, a study was made on the action of the unfiltered light from a quartz mercury lamp on a solution of ferric sulphate acidified with sulphuric acid. It was found that there was sufficient reduction to give a strong test for ferrous ions. This is in direct confirmation of the work of Ross[43]. A quantitative study of extent of the reduction showed that even after six hours of irradiation of duplicate samples of 40 cc. of 0.0467 molar ferric sulphate solution, there was only 0.6% reduction. Further irradiation did not increase this value. It was found, however, that when a solution of ferrous sulphate, acidified with sulphuric acid, was irradiated for the same length of time in the absence of air, there was slight but sufficient oxidation to give a good positive test for ferric ions. It was impossible to obtain any appreciable oxidation, even though irradiation was continued considerably beyond six hours. This indicates that this is not a true equilibrium reaction between ferric sulphate and ferrous sulphate when exposed in the absence of air to unfiltered ultraviolet light. Consequently, it was concluded that since full radiation was used, there

is undoubtedly a particular wave length or range which is specific for each reaction.

Next, a "dark reaction" was carried out, letting duplicate samples, consisting of 5 cc. of 0.1835 M ferric sulphate, 10 cc. of 4 Molar formic acid, and 25 cc. of carbon dioxide - free water, to stand for 47 hours in the dark. Analysis showed that there was no reduction of the iron salt, no decomposition of formic acid, and no liberation of carbon dioxide. The reaction under the influence of light is, therefore, truly photochemical as defined by Benrath[58].

A solution of a "blank", containing formic acid only, and a solution of the "sample", containing ferric sulphate with formic acid, were then irradiated for a period of 26 hours. The "blank" was composed of 10 cc. of 4 M HCOOH and 30 cc. of CO_2 free water, while the "sample" contained 5 cc. of 0.1835 M ferric sulphate, 10 cc. 4 M HCOOH, and 25 cc. of water. Qualitative tests made on the reaction mixtures after irradiation showed that formaldehyde was present in the "blank" but <u>not</u> in the "sample". The presence of formaldehyde was demonstrated by Von Fillinger's[59] test as follows: To 5 cc. of the solution to be analyzed is added 5 cc. of the reagent (0.3% Witt's peptone solution containing 10 drops of 5% $FeCl_3$ in 100 cc.) The solution is then underlayed with 5 cc. of concentrated sulphuric acid. The development

of a red to violet colored ring, depending on the amount of formaldehyde present constitutes a positive test.

The carbon dioxide formed by the decomposition in the "blank" exceeded the quantity from the the sample. Because of this latter fact and also the formation of formaldehyde in the "blank", it was concluded that the nature of the decomposition of formic acid in the presence of ferric sulphate must be different from that in its absence. The decomposition of formic acid in the presence of ferric sulphate may be more aptly defined as a photochemical oxidation of the formic acid by ferric sulphate, especially since the latter is completely reduced as has been shown in the quantitative investigation to be described later.

C. Experimental Method

H. S. Fry and E. G. Gerwe[51], in studying the decomposition of citric acid in the presence of ferric sulphate, apparently assumed that the extent of the decomposition of citric acid in the "sample" in each experiment was represented by the difference between the amount of carbon dioxide liberated from the "sample" and that liberated from the blank. However, as shown in the preliminary experiments of the present study, this was not the case with formic acid. Hence it is quite evident that the photolysis of formic acid and in the presence of

ferric sulphate must be treated and studied as two separate processes.

Kahlbaum's formic acid, specific gravity 1.22, yielded a fraction distilling between 101-103°C. This distillate was used to prepare the approximately 4 M. solution of formic acid used in this study. A ferric sulphate solution, made approximately 0.2 M and acidified with sulphuric acid, was used as the stock iron solution. This was standardized against permanganate solution after previous reduction using Kahlbaum's finely divided magnesium. All water for dilution purposes was freshly boiled to insure complete absence of carbon dioxide.

Reaction mixtures for the "blank" were made up immediately preceding irradiation, using 10 cc. of the stock formic acid solution and 30 cc. of carbon dioxide-free water. That for the "sample" consisted of the same quantity of formic acid, a definite known quantity of standard ferric sulphate solution, and sufficient water to make the volume up to 40 cubic centimeters.

Before beginning irradiation, the entire train, including the reaction units, was swept out with nitrogen to insure a carbon dioxide free train before connecting the ascarite towers. The nitrogen was previously washed by passing it through concentrated sulphuric acid and then ascarite. The nitrogen has a two-fold purpose:

first, to keep the reaction mixture thoroughly agitated and thus aid in obtaining uniform absorption of light; and second, to sweep out the carbon dioxide liberated by the reaction.

Irradiation in the case of the "samples" was continued until the ferric sulphate had been completely reduced. The potential across the lamp was maintained in all experiments at 50 volts with an amperage of 3.8. After discontinuing irradiation, the entire train was swept out until the ascarite towers reached constant weight. Thus, the carbon dioxide evolved from the reaction was the difference between the weights of the ascarite tower before and after irradiation. Since a known quantity of ferric sulphate was always added to the reaction mixtures of the "samples" and since irradiation was stopped upon complete reduction to the ferrous state, the exact quantity of ferric sulphate entering into the reaction was known without further analysis. The quantity of formic acid decomposed was determined by difference, using the Mercuric Chloride Method[60] with some modifications as shown below.

Determination of Formic Acid by a Modified Mercuric Chloride Method

In the solutions to be analyzed in addition to the formic acid, small amounts of formaldehyde were

present in the blank, while the sample contained the excess formic acid, ferrous sulphate, and also sulphuric acid. The method as described in the literature was not standardized with a view to the determination of formic acid in solutions containing these impurities. Hence, it was necessary to modify the method mentioned above to allow for the removal of the ferrous sulphate, and in addition to test the applicability of the modified method for the determination of formic acid in the presence of small amounts of formaldehyde and sulphuric acid. The standard test solutions were made up as nearly as possible identical in composition to the aliquot portions of the solutions to be analyzed.

The method in brief is as follows: To the standard solutions made up as shown in Table I and placed in a 250 cc. Erlenmeyer flask is added 10 cc. of water and 5 cc. of 1 N NaOH, which is in slight excess. The ferrous hydroxide formed is almost instantaneously oxidized in air to the ferric hydroxide. This latter is filtered on a small filter paper and the residue washed thoroughly. The filtrate is then exactly neutralized with 0.1 N H_2SO_4 after which the usual Mercuric Chloride Method is followed. Thus, 10 cc. of 30% sodium acetate are next added and then 25 cc. of 10% mercuric chloride. After heating the solutions for two hours in a boiling water bath and subse-

quent cooling, the precipitated mercurous chloride is filtered into a weighed gooch grucible, washed thoroughly first with water, then 95% alcohol, and finally with ether. The mercurous chloride is then dried further by heating at 110° in an oven, and weighed. From this weight, is calculated the equivalent quantity of formic acid.

The results, using solutions of known composition, are listed in Table I.

TABLE I

1	2	3	4	5	6	7	8	9	10	11	12	13	14
#	Mohr's Salt	HCOOH added about .2N	H_2SO_4 .0965N	HCHO added	NaOH 1N	$HgCl_2$ 10%	Crux + HgCl	Crux alone	HgCl	HCOOH =#10 F=.0976	HCOOH added actual	% Theory #11 ÷ #12 x 100	Aver. % Theory
	gms.	cc.	cc.	gms.	cc.	cc.	gms.	gms.	gms.	gms.	gms.		
1	-	10	-	-	5	25	13.6663	12.7515	.9148	.0893	Av. .0894	100%	
2	-	10	-	-	5	25	13.1439	12.2268	.9171	.0895		100.0	
3	.0737	10	11	-	5	25	13.8036	12.8970	.9066	.0885	.0894	99.0	
4	.0737	10	11	-	5	25	13.4115	12.4972	.9143	.0892	.0894	99.8	99.35
5	.0737	10	11	-	5	25	13.2224	12.3116	.9108	.0889	.0894	99.4	
6	.0737	10	11	-	5	25	12.9967	12.0885	.9082	.0886	.0894	99.2	
7	-	10	-	-	5	25	14.6779	13.8035	.8744	.0853	.0852	100.0	
8	-	10	-	-	5	25	13.4412	12.5688	.8724	.0851			
9	.0737	10	11	-	5	25	13.5050	12.6303	.8747	.0853	.0852	100.10	99.99
10	.0737	10	11	-	5	25	14.2326	13.3695	.8731	.0851	.0852	99.88	
11	.0737	10	11	.06	5	25	14.1235	13.2461	.8774	.0855	.0852	100.3	100.09
12	.0737	10	11	.06	5	25	14.2531	13.3804	.8727	.0851	.0852	99.88	
13	.0737	-	11	-	5	25	no precipitate						

The results thus show that the method is adaptable to the determination of formic acid in the presence of small quantities of sulphuric acid, ferrous or ferric sulphate, and small quantities of formaldehyde such as might be found in the reaction mixtures to be analyzed. It may be mentioned that solutions containing more than 0.1 gram of formaldehyde per aliquot sample or greater than 0.10% in the final diluted sample will cause erroneous results, since the reduction of mercuric chloride solutions in solutions containing more than 0.10% of formaldehyde is appreciable.

D. Photolysis of Formic Acid

As mentioned previously, preliminary experiments indicated that the mechanism of the decomposition of formic acid by ultraviolet light in the absence of ferric sulphate is entirely different from that in the presence of this salt. This conclusion is based upon the following experimental facts:

(1) Formaldehyde is one of the decomposition products in the absence of ferric sulphate but not in its presence.

(2) For the same duration of irradiation, more formic acid is decomposed in the absence of the ferric salt than in its presence.

(3) For the same duration of irradiation, less carbon dioxide is evolved in the absence of the ferric salt than in its presence.

(4) When formic acid alone is irradiated, the molar ratio of carbon dioxide evolved to formic acid decomposed, as has been found in this study, is 1.00 : 1.84; while when irradiated in the presence of the ferric salt, the ratio is 1.00 : 0.97.

Hence, it was obviously necessary to make separate studies of the decomposition in the absence of the ferric salt and in its presence.

In connection with this work, it is advisable to again draw attention to the research of Allmand and Reeves[54], whose contributions to the field of Photochemistry are not only important but also of a very exact nature. Moreover, as a consequence of their study of the photolysis of formic acid in aqueous solutions, Allmand and Reeves postulate four reactions, in which the first two are called primary and the second two secondary.

Primary Reactions:

$$(a_1)\quad HCOOH \longrightarrow 2\,H' + CO_2$$

$$(b_1)\quad HCOOH \longrightarrow HOH + CO'$$

Secondary Reactions:

$$(a_2)\quad HCOOH + 2\,H' \longrightarrow HCHO + HOH$$

$$(b_2)\quad HCOOH + CO' \longrightarrow HCHO + CO_2$$

It will be remembered that since practically no hydrogen or carbon monoxide was liberated in the case of more concentrated solutions of formic acid (2.40 molar),

and since formaldehyde was formed as one of the decomposition products, these workers postulated the above four reactions. On the other hand, since, in the case of the more dilute formic acid solution (0.113 molar), practically no formaldehyde was formed, and since hydrogen and carbon monoxide were liberated, Allmand and Reeves concluded that the secondary reactions occur only in the more concentrated solutions. Further, on the basis of quantitative determinations, they concluded that the speed of reaction (a_1) is six times greater than that of reaction (b_1).

For the purpose of obtaining a comparison between the photochemical decomposition of formic acid in the absence and in the presence of ferric sulphate, as well as to check the work of Allmand and Reeves, duplicate samples of 0.93 molar formic acid were irradiated for 32 hours.

Qualitative tests showed that in no case was carbon monoxide liberated. The test applied was that which has been suggested by Levy and Pecoul[61]. The liberated gases are passed through a tube containing iodine pentoxide (temperature 100° C.). Any carbon monoxide present reduces the iodine pentoxide with liberation of free iodine which is swept into a tube of chloroform. The development of a pink to rose color is a positive test for carbon monoxide. This test is reputed to detect carbon monoxide in air at a concentration of one

part in ten thousand. The absence then of carbon monoxide is in complete agreement with the results obtained by Allmand and Reeves when they irradiated the 2.40 molar formic acid.

The quantity of formic acid decomposed in each case was determined by difference according to the following procedure and by means of the method previously described. The solution in each reaction tube after irradiation was diluted to 200 cc. and aliquot portions of 10 cc. each were analyzed for the formic acid content. Exactly the same quantity of stock formic acid solution as that subjected to irradiation was likewise diluted to 200 cc. and 10 cc. aliquot portions taken for analysis. Analysis of both solutions was made simultaneously and the difference in formic acid content of the two solutions gave the measure of the formic acid decomposed by irradiation. The method gave excellent check results and the particular procedure employed undoubtedly gives exceptionally accurate values.

The results of this experiment may be more easily understood by a study of the data listed in the tables shown below. Table II is a summary of the results of experiment $A_{I\ \&\ II}$, including all conditions, etc., while Table III is a record of the formic acid analysis for the same experiment. Experiment $B_{I\ \&\ II}$ was recorded in exactly the same manner. The complete summary of this experiment on the photolysis of formic acid, including all calculations is embodied in Table IV.

TABLE II

Record of Experiment A, Run in Duplicate

#		A_I	A_{II}
1	Composition	10 cc. Stock formic acid approx. 1 Molar 30 cc. CO_2-free water	Duplicate
2	Time	10/8/1931 9:15 P.M. - 10/9/1931 5:15 P.M. 32 hours	
3	Conditions	50 volts across lamp 3.7 amperes 29°C. temp. of reaction mixtures	N_2 bubbled thru reaction mixture continuously
4	Wgt. of ascarite tower after	66.6817 grams	64.5726 grams
5	Wgt. of ascarite tower before	66.6331 grams	64.5267 grams
6	Gms. CO_2 absorbed	0.0486 grams	0.0459 grams
7	HCOOH before irradiation	1.7066 grams	1.7066 grams
8	HCOOH after irradiation	1.6152 grams	1.6184 grams
9	HCOOH decomposed	0.0914 grams	0.0882 grams

TABLE III

Formic Acid Analysis

1	2	3	4	5	6	7	8	9	10	11	12
#	Aliquot sample HCOOH soln. cc.	NaOH 1N cc.	NaAc soln. 30% cc.	HCl dil. cc.	$HgCl_2$ 10% soln. cc.	Gms. HgCl + crux	Gms. crux -	Gms. HgCl #7-#8	Gms. HCOOH = #9 F=.0976	Aver. HCOOH gms.	gms. HCOOH in total soln. (aliquotx20)
					# A_I	HCOOH analysis after irradiation					
1	10	5	10	2	25	13.5237	12.6954	.8283	.08084)		
2	10	5	10	2	25	13.3279	12.5008	.8271	.08073)	.08076	1.6152
3	10	5	10	2	25	13.1052	12.2783	.8269	.08071)		
					# A_{II}	HCOOH analysis after irradiation					
4	10	5	10	2	25	14.0004	13.1711	.8293	.08094)		
5	10	5	10	2	25	13.6461	12.8164	.8297	.08098)	.08092	1.6184
6	10	5	10	2	25	12.7287	11.9004	.8283	.08084)		
					Control	HCOOH analysis before irradiation					
7	10	5	10	2	25	13.3718	12.4989	.8729	.08518)	.08533	1.7066
8	10	5	10	2	25	13.0485	12.1727	.8758	.08548)		

TABLE IV

Reactions:

Primary

(a_1) $HCOOH \longrightarrow 2H' + CO_2$

(b_1) $HCOOH \longrightarrow CO' + HOH$

Secondary

(a_2) $HCOOH + 2H' \longrightarrow HCHO + HOH$

(b_2) $HCOOH + CO' \longrightarrow HCHO + CO_2$

1	2	3	4	5	6	7	8
	CO_2 Liberated			HCOOH Decomposed			Molar Ratio
Run	Exptl.	Theory		Theory	Exptl.	% of Theory	
	Milli-moles	per (a_1) Milli-moles	per (b_2) Milli-moles	Milli-moles	Milli-moles	(#6÷#5)x100	CO_2:HCOOH From #2 & #6
A_1	1.11 + .02	0.95	0.16	2.21	1.99 - .02	90.1 - 1.8	1.00 : 1.80
A_2	1.04 - .05	0.89	0.15	2.09	1.92 - .09	91.9 ± 0.0	1.00 : 1.85
B_1	1.12 + .03	0.96	0.16	2.24	2.07 + .06	92.4 + 0.5	1.00 : 1.85
B_2	1.10 + .01	0.94	0.16	2.19	2.04 + .03	93.2 + 1.3	1.00 : 1.86
Aver.	1.09 ± .03	0.94	0.16	2.18	2.01 - .05	91.9 ± 0.9	1.00 : 1.84

Discussion of Results

The theoretical values shown in Table II were calculated on the basis of the equations postulated by Allmand and Reeves and also assuming their ratio of 6 : 1 for the relative speeds of reactions (a_1) and (b_1). The theoretical quantity of formic acid decomposed (column #5) was calculated from the amount of carbon dioxide experimentally determined. Deviations are listed to the right in columns #2, #6, and #7.

The validity of the method of calculation and of the assumption of the equations postulated by Allmand and Reeves is based upon the following facts:

(a) The formic acid decomposes with evolution of carbon dioxide.

(b) Formaldehyde is one of the products of the decomposition and can only be so formed according to reaction (a_2) or (a_2) and (b_2).

(c) Reaction (b_1) is concluded to take place on acceptance of the work of Berthelot and Gaudechon[53] and especially of Allmand and Reeves[54].

(d) Since no carbon monoxide was liberated, as shown by the extremely delicate test previously described, reaction (b_2) must go to completion.

Column #8 of Table IV represents the stoichiometrical ratio of the milli-moles of carbon dioxide evolved by the decomposition to the milli-moles of formic acid

decomposed. The average value of this ratio is shown to be 1.00 : 1.84, while the corresponding theoretical value, as determined from the equations or from column #2 and #5, is 1.00 : 2.00. The experimental results are thus about 92 per cent of the theoretical. The divergence of 8% from the theoretical value might be traced to two probable sources, either to the experimental error almost unavoidably connected in the methods of analysis involving such small quantities of materials determined, or to the deactivation and subsequent escape of a part of the hydrogen in the molecular state. According to the work of Allmand and Reeves, this latter is quite likely to occur in solutions of formic acid, the concentration of which is appreciably less than two molar.

It might be well to call to attention the fact that the experimental results agree equally as well if we assume the decomposition of formic acid to be represented by equations (a_1) and (a_2), the sum total of which can be represented by the equation shown below.

(a_1) $\quad HCOOH \longrightarrow 2H' + CO_2$

(a_2) $\quad HCOOH + 2H' \longrightarrow HCHO + HOH$

(a_1)+(a_2) $\quad 2HCOOH \longrightarrow HCHO + HOH + CO_2$

Thus, the stoichiometrical ratio of 1:00 to 1.84 may equally well establish the above equation, but this

conception was rejected on the basis of Allmand and Reeves' identification of carbon monoxide as one of the decomposition products when fairly dilute solutions of formic acid are irradiated.

Whereas the above workers have established equations (a_1), (b_1), (a_2), and (b_2) as a result of analysis of the gaseous products liberated, this work confirms this theory of the photochemical decomposition of formic acid in aqueous solution, as a result of the determination of the carbon dioxide liberated and the formic acid decomposed.

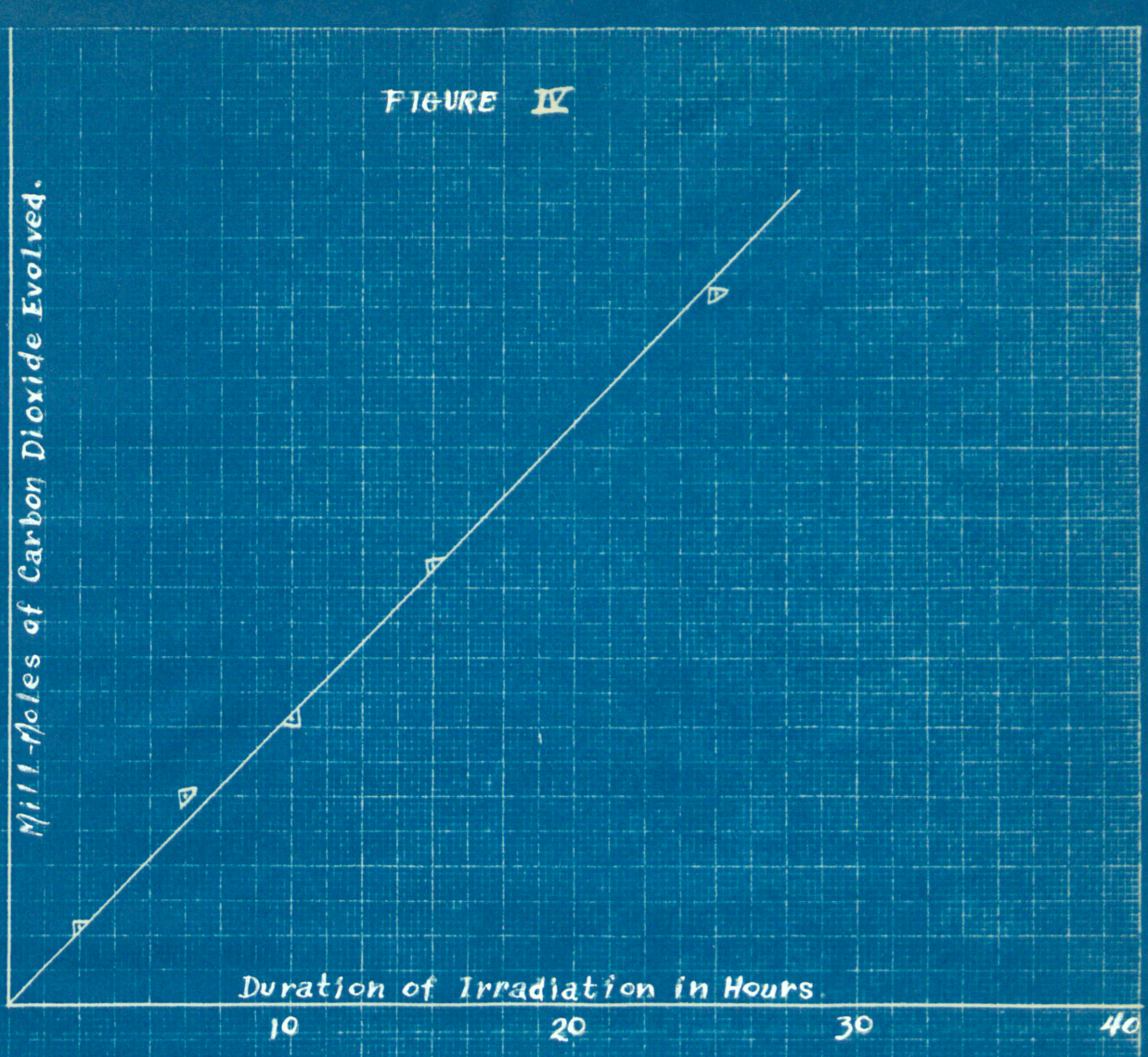
Additional facts of value for comparing the reactions involved in the photolysis of formic acid and those involved in its photochemical oxidation by ferric sulphate, have been obtained by a study of the "Change-Time" curves representing the respective decompositions. This comparison will be discussed later.

The "Change-Time" curve for formic acid alone was obtained in the manner described below.

Separate solutions of the same molarity were irradiated in duplicate for different periods of time, and the quantities of carbon dioxide liberated were plotted in milli-moles as ordinate against time of irradiation in hours as abscissa.

The results of this experiment are summarized in Table V and Figure IV.

FIGURE IV



Change--Time Curve.

For the Photolysis of Formic Acid.

TABLE V

Photolysis of Aqueous Formic Acid Solutions for Different Periods of Irradiation (50 volts, 3.8 amperes)

Exp.	Time of Irradiation Hrs.	Temp. C.	Wgt. of Ascarite Towers gms. After	Wgt. of Ascarite Towers gms. Before	CO_2 Evolved gms.	CO_2 Evolved Average gms.	CO_2 Evolved Average milli-moles	Values of k c/t = k
A_1	2.50	28°	70.8202	70.8149	.0053	.0050	0.114	.046
A_2			70.4456	70.4409	.0047			
B_1	6.25	29°	70.7429	70.7307	.0122	.0131	0.298	.048
B_2			70.3678	70.3539	.0139			
C_1	10.00	28°	70.7307	70.7128	.0179	.0179	0.407	.041
C_2			70.3539	70.3359	.0180			
D_1	15.00	28°	70.8149	70.7876	.0273	.0275	0.625	.042
D_2			70.4409	70.4131	.0278			
E_1	25.00	29°	70.7876	70.7429	.0447	.0450	1.023	.041
E_2			70.4131	70.3678	.0453			

Thus, the curve obtained when the values of time are plotted as absicissae against milli-moles of formic acid decomposed as ordinates, is a straight line function. If we represent the milli-moles of formic acid decomposed by (C), and the time of irradiation by (t), then (C) is proportional to (t). From this, then, we can write the equation for the straight line passing through the origin as $C = kt$, where the constant (k) represents the slope. The last column of Table V contains values for k for each particular solution. The fact that k is shown to be a constant, is additional evidence that the quantity of formic acid is directly proportional to the time of irradiation. This will be discussed further along with the "Change-Time" curves for the photochemical oxidation of formic acid.

E. Photochemical Oxidation of Formic Acid by Ferric Sulphate

In this experiment, designed to study the photochemical oxidation of formic acid by ferric sulphate solutions in duplicate consisting of 10 cc. of approximately 1 molar formic acid, 5 cc. of 0.1835 molar ferric sulphate, and 25 cc. of carbon dioxide-free water were irradiated with the full light from the quartz mercury lamp. Thus, the volume of the solutions in each tube irradiated was in all cases 40 cc. The distance between the lamp and the reaction

tubes was constant at 15 cm., the temperature maintained as nearly as possible at 28°-33° C., the voltage across the lamp at 50 volts, and the intensity of the current at 3.6 - 3.8 amperes. Irradiation was continued in all cases until complete reduction of the ferric salt, while the carbon dioxide liberated and the quantity of formic acid decomposed were determined according to the method described in detail in Part C, page 45 of this thesis. The results of five duplicate determinations are summarized in Table VI below. Table VII contains the results of three duplicate observations in which the concentration of ferric sulphate is just half of that used in experiment $E_{(a)}$ recorded in Table VI. Calculations embodied in Tables VI and VII are based upon the two reactions represented by equations (a) and (b), which will be discussed shortly.

TABLE VI

Photochemical Oxidation of Formic Acid by Ferric Sulphate

(a) $Fe_2(SO_4)_3 + HCOOH \longrightarrow 2FeSO_4 + H_2SO_4 + CO_2$

(b) $HCOOH \longrightarrow H_2 + CO_2$

Expt. $E_{(a)}$

1	2	3	4	5		6	7
Expt.	Milli-moles $Fe_2(SO_4)_3$	Hrs. of Irradia-tion	Temp. of Reaction Tubes C.	Milli-moles HCOOH Decomposed			
				Exptl.		Theory per (a) = #2	Theory per (b) #5 - #6
I_1	0.92	32	28°	1.26	-.05	0.92	0.34
I_2	"	"	"	1.27	-.04	"	0.35
II_1	"	"	"	1.29	-.02	"	0.37
II_2	"	"	"	1.29	-.02	"	0.37
III_1	"	"	32°	1.33	+.02	"	0.41
III_2	"	"	"	1.33	+.02	"	0.41
IV_1	"	"	"	1.33	+.02	"	0.41
IV_2	"	"	"	1.33	+.02	"	0.41
V_1	"	"	33°	1.36	+.05	"	0.44
V_2	"	"	"	1.26	-.05	"	0.34
Aver.	"	"	-	1.31	$\pm$.03	"	0.39

TABLE VI

Photochemical Oxidation of Formic Acid by Ferric Sulphate

(a) $Fe_2(SO_4)_3 + HCOOH \longrightarrow 2FeSO_4 + H_2SO_4 + CO_2$

(b) $HCOOH \longrightarrow H_2 + CO_2$

Expt. $E_{(a)}$

8	9	10	11		12		13
Milli-moles CO_2 Liberated					CO_2 % of Theory (#11 ÷ #10) x 100		Molecular Ratio CO_2 : HCOOH
Theory			Exptl.				
per (a) ⌒ #6	per (b) ⌒ #7	Total #8 + #9					Exptl.
0.92	0.34	1.26	1.19	-.08	94.5	-2.6	1.00 : 0.95
0.92	0.35	1.27	1.23	-.04	96.9	-0.2	1.00 : 0.97
"	0.37	1.29	1.19	-.08	92.3	-4.8	1.00 : 0.92
"	0.37	1.29	1.23	-.04	95.4	-1.7	1.00 : 0.95
"	0.41	1.33	1.33	+.06	100.0	+2.9	1.00 : 1.00
"	0.41	1.33	1.35	+.08	101.5	+4.4	1.00 : 1.02
"	0.41	1.33	1.32	+.05	99.3	+2.2	1.00 : 0.99
"	0.41	1.33	1.32	+.05	99.3	+2.2	1.00 : 0.99
"	0.44	1.36	1.26	-.01	92.7	-4.4	1.00 : 0.93
"	0.34	1.26	1.25	-.02	99.2	+2.1	1.00 : 0.99
"	0.39	1.31	1.27	±.05	97.1	±2.75	1.00 : 0.97

TABLE VII

Photochemical Oxidation of Formic Acid with Half-concentration (.46 Milli-moles) of Ferric Sulphate

(a) $Fe_2(SO_4)_3 + HCOOH \longrightarrow 2FeSO_4 + H_2SO_4 + CO_2$

(b) $HCOOH \longrightarrow H_2 + CO_2$

Expt. $E_{(b)}$

1	2	3	4	5		6	7
Expt.	Milli-moles $Fe_2(SO_4)_3$	Hrs. of Irradiation	Temp. of Reaction Tubes C.	Milli-moles HCOOH Decomposed			
				Exptl.		Theory per (a) = #2	Theory per (b) #5 - #6
I_1	0.46	9.5	32°	0.61	-.01	0.46	0.15
I_2	"	"	32°	0.58	-.04	0.46	0.12
II_1	"	"	28°	0.64	+.02	"	0.18
II_2	"	"	28°	0.61	-.01	"	0.15
III_1	"	"	28°	0.64	+.02	"	0.18
III_2	"	"	28°	0.65	+.03	"	0.19
Aver.	0.46	9.5	-	0.62	±.02	0.46	0.16

TABLE VII

Photochemical Oxidation of Formic Acid with Half-concentration (.46 Milli-moles) of Ferric Sulphate

(a) $Fe_2(SO_4)_3 + HCOOH \longrightarrow 2FeSO_4 + H_2SO_4 + CO_2$

(b) $HCOOH \longrightarrow H_2 + CO_2$

Expt. $E_{(b)}$

8	9	10	11		12		13
Milli-moles CO_2 Liberated					CO_2 % of Theory (#11 ÷ #10) x 100		Molecular Ratio CO_2:HCOOH
Theory			Exptl.				
per (a) ≙ #6	per (b) ≙ #7	Total #8+#9					Exptl.
0.46	0.15	0.61	0.60	+.00	98.4	+1.3	1.00 : 0.98
"	0.12	0.58	0.57	-.03	98.3	+1.2	1.00 : 0.98
"	0.18	0.64	0.62	+.02	96.9	-0.2	1.00 : 0.97
"	0.15	0.61	0.60	+.00	98.4	+1.3	1.00 : 0.98
"	0.18	0.64	0.62	+.02	96.9	-0.2	1.00 : 0.97
"	0.19	0.65	0.61	+.01	93.8	-3.3	1.00 : 0.94
0.46	0.16	0.62	0.60	±.01	97.1	±1.2	1.00 : 0.97

The quantities of ferric sulphate listed in column #2 of Tables VI and VII represent the quantities of the ferric salt used in each reaction mixture. Then, since irradiation was continued until this salt was completely reduced, the theoretical amount of formic acid decomposed per equation (a), (column #6), will be equivalent to the quantity of ferric salt used. The values listed in column #7 are obtained by subtracting from the figures in #5 those of column #6, and represent the quantity of formic acid decomposed per equation (b). The molecular ratio of the carbon dioxide evolved to the formic acid decomposed, according to equations (a) and (b), are 1.00 : 1.00; hence, if all quantities are represented in milli-moles, then the values in columns #8 and #9 will be exactly equal to those in #6 and #7. The theoretical per cent of carbon dioxide (column #12) is obtained from columns #10 and #11. The experimentally determined molecular ratios of column #13 are obtained from columns #5 and #11.

Discussion of Results

Part D of this paper contained some discussion and presented some experimental evidence which showed that the photolysis of formic acid is entirely different from the photochemical oxidation of formic acid by ferric sulphate. In this, it was shown that formaldehyde was

present as one of the products of decomposition in the former but not in the latter; a greater quantity of formic acid is decomposed but less carbon dioxide is evolved in the former decomposition than in the latter. In experiment E, additional evidence is presented which more completely establishes this difference and which also establishes the equations postulated to explain the reactions involved in the photochemical oxidation of formic acid by ferric sulphate.

In addition to the reactions postulated for the mechanism of this decomposition and which have been experimentally confirmed, on the basis of theoretical speculations it is possible to suggest two other mechanisms. For convenience, the latter two will be designated II and III, an analysis of which should be made to ascertain their worthiness and to avoid the criticism of omitting considerations of other possible mechanisms.

It is theoretically possible that, in the photochemical oxidation of formic acid, this compound might decompose according to the reactions postulated by Allmand and Reeves and confirmed by the authors of this paper. On the basis of this mechanism, it may be reasoned that the ferric sulphate is subsequently reduced by the formaldehyde formed by secondary reactions (a_2) and (b_2), according to the following equations:

(a_1) $HCOOH \longrightarrow 2H' + CO_2$

(b_1) $HCOOH \longrightarrow CO' + HOH$

(a_2) $HCOOH + 2H' \longrightarrow HCHO + HOH$

(b_2) $HCOOH + CO' \longrightarrow HCHO + CO_2$

(c) $Fe_2(SO_4)_3 + HCHO + H_2O \longrightarrow 2FeSO_4 + H_2SO_4 + HCOOH$

This theory is, however, proven to be erroneous on the basis of the following facts:

(1) At no stage of the experiment was it possible to detect any formaldehyde, or carbon monoxide.

(2) The amount of formic acid decomposed (experiment $E_{(a)}$) would require the reduction of 1.31 milli-moles of ferric sulphate, whereas only 0.92 milli-moles were actually used.

(3) The "Change-Time" curves, which will be discussed later, show conclusively that the actual decomposition cannot be analogous to the decomposition by photolysis.

According to theory III, it is possible to represent the decomposition according to the following set of equations:

(a_1) $HCOOH \longrightarrow 2H' + CO_2$

(b_1) $HCOOH \longrightarrow CO' + HOH$

(c) $Fe_2(SO_4)_3 + 2H' \longrightarrow 2FeSO_4 + H_2SO_4$

(d) $Fe_2(SO_4)_3 + CO' + H_2O \longrightarrow 2FeSO_4 + H_2SO_4 + CO_2$

That this theory is not compatible with the experimental results is shown by the facts briefly stated below:

(1) It is reasonable to suppose that some molecular hydrogen or carbon monoxide would become activated by radiations from a quartz mercury lamp. However, even though, in previously conducted experiments, as much as five liters of each of these gases were passed through separate samples of ferric sulphate solutions in the presence of ultraviolet light and during a period of ten hours, there was no reduction of the ferric salt beyond that due to the action of the light alone.

(2) In further refutation of this theory, only 0.92 milli-moles of ferric sulphate was used (experiment $E_{(a)}$), whereas 1.31 milli-moles would be required on the basis of the quantity of formic acid decomposed.

(3) This theory is, moreover, rejected on the evidence presented by the study of the "Change-Time" curves.

Hence, on the basis of experimental evidence, the above theories II and III are invalidated, while theory I is shown to satisfactorily explain the mechanism of the photochemical oxidation of formic acid. This will be discussed further at this time. In other words, according to theory I, the mechanism of the decomposition is represented by the following reactions:

(a) $Fe_2(SO_4)_3 + HCOOH \longrightarrow 2FeSO_4 + H_2SO_4 + CO_2$

(b) $HCOOH \longrightarrow H_2 + CO_2$

The following experimental facts, which are summarized in Tables VI and VII, substantiate this theory:

(1) The quantity of carbon dioxide evolved is 97.1 per cent of the theoretical amount calculated on the basis of this theory.

(2) This theory is compatible with the experimentally determined molecular ratio of carbon dioxide evolved to formic acid decomposed. Column #13 of Tables VI and VII show this ratio to be:

$$CO_2 : HCOOH :: 1.00 : 0.97$$

(3) Reactions (a) and (b) must be concurrent reactions. In addition to the evidence recorded in the above tables, experiments, previously described, have shown that it is unlikely that hydrogen could be the active reducing agent for the iron salt. Hence, the possibility of reaction (b) being primary with subsequent reduction of ferric sulphate by hydrogen, is rejected. Moreover, in connection with this point, this theory is substantiated by the "Change-Time" curves.

(4) Further, the oxidation-reduction reaction represented by equation (a) is more reasonable from the viewpoint of the chemical properties of these compounds.

In the following Part $E_{(c)}$ of this section, a study of the "Change-Time" curves is presented which affords additional experimental evidence in substantiation of this theory.

E(c). Change-Time Curves

Conditions with respect to temperature of the reaction-tubes, distance between the quartz mercury lamp and the tubes, potential across the lamp, and intensity of current were maintained as nearly as possible identical with those of all previous experiments. The reaction mixtures in each sample irradiated contained respectively the quantity of ferric sulphate designated in Table VIII, columns #3 and #4, 10 cc. of approximately 4 molar formic acid solution, and sufficient carbon dioxide-free water to bring the volume in each case up to 40 cc. As in previous experiments, described in Section E, irradiation was continued until all of the ferric sulphate had been reduced. The absence of ferric ions was demonstrated by the inability of the solution to give a positive test with potassium sulphocyanate.

Curve (1) of Figure V was obtained by plotting the milligrams of carbon dioxide evolved as ordinate against the time of irradiation in hours as abscissa. Curve (2) is obtained by plotting in a like manner the milli-moles of ferric sulphate reduced against time in hours. The data from which the curves in Figures V and VI are plotted are recorded in Table VIII.

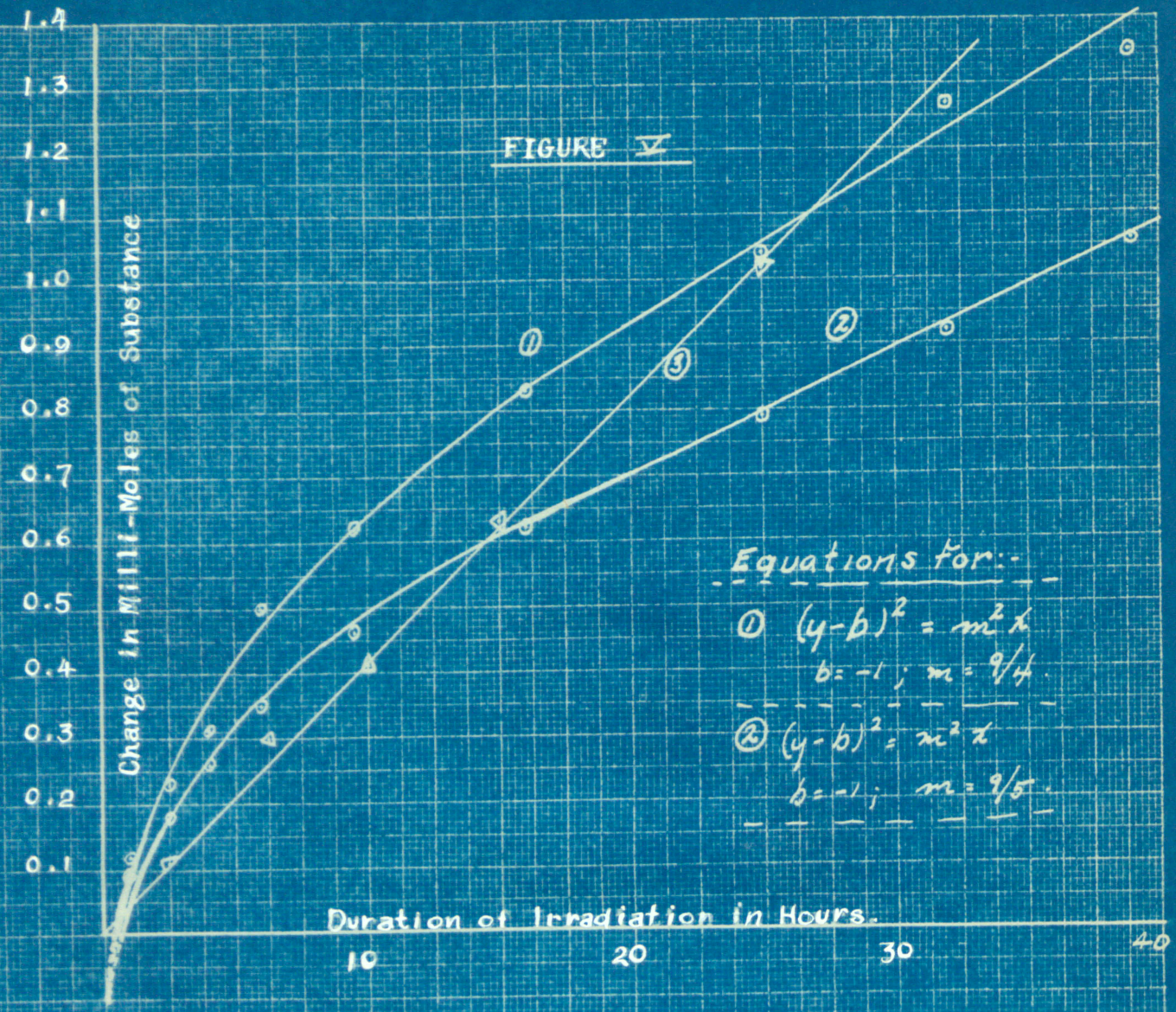
Curves (1) and (2) of Figure V are parabolic in nature, having the same origin. The fact that curve (1)

TABLE VIII

Change-Time Curves for the Photochemical Oxidation of Formic Acid by Ferric Sulphate

1	2	3	4	5	6	7	8
Expt.	Temp. of Reaction Tubes	Ferric sulphate reduced Gms.	Milli-moles	CO_2 Evolved Gms.	Milli-grams	Time of Irradt'n. Hrs.	$(\text{Time})^{1/2} = T^{1/2} = x$
1	28°C.	0.0552	0.09	0.0053	0.12	1.0	1.00
2	"	0.0705	0.18	0,0103	0.23	2.5	1.55
3	"	0.1057	0.26	0.0138	0.31	4.0	2.00
4	"	0.1410	0.35	0.0221	0.50	6.0	2.45
5	"	0.1833	0.46	0.0271	0.62	9.5	3.08
6	"	0.2467	0.62	0.0364	0.83	16.0	4.00
7	"	0.3172	0.79	0.0456	1.04	25.0	5.00
8	"	0.3665	0.92	0.0558	1.27	32.0	5.66
9	"	0.4229	1.06	0.0593	1.35	39.0	6.25

FIGURE V



Equations for:-

① $(y-b)^2 = m^2 x$

$b = -1$; $m = 9/4$.

② $(y-b)^2 = m^2 x$

$b = -1$; $m = 9/5$.

CHANGE-TIME CURVE.

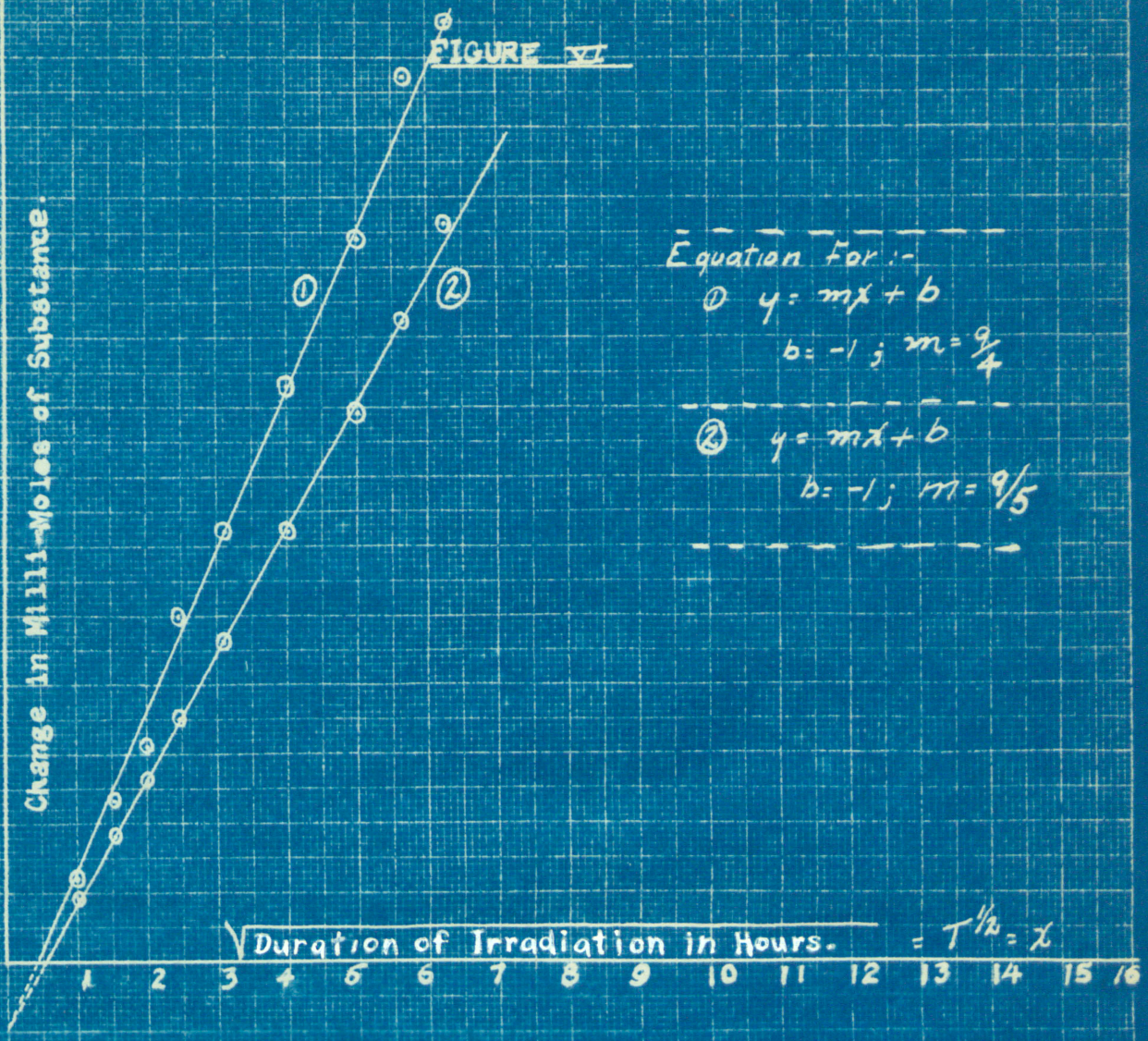
For the Photochemical Oxidation of Formic Acid

By Ferric Sulphate.

Curve (1) represents milli-moles of carbon dioxide evolved.

Curve (2) " " " " ferric Sulphate reduced.

Curve (3) represents the milli-moles of carbon dioxide evolved in the photolysis of formic acid.



CHANGE--TIME CURVE.

Parabolic Curves (1) and (2) of Figure V Converted to Straight Lines by Plotting the values per Equation:-

$$y = x_1^{1/2}$$

$$x_1^{1/2} = T^{1/2} = x$$

is a part of a broader parabola than is curve (2), though similar in character, may be expected since the molecular ratio of carbon dioxide evolved to ferric sulphate reduced is 1.3 : 1.00. If a like curve were plotted for the formic acid decomposed, it would be identical to #(1), since the molecular ratio of carbon dioxide evolved to the formic acid decomposed is 1.00 : 1.00. A more important feature, however, is brought out by the distinct contrast between curves (1) and (2) and curve (3), previously noted in Part D. The latter is a straight line which passes through the origin, while, as just mentioned, the former are parabolic curves. This extreme difference in the character of the two types of curves seems to be conclusive evidence of the difference in the kind of decomposition of formic acid by photolysis and by photochemical oxidation.

Curves (1) and (2) are shown to be parabolic by the fact that, when the data upon which they are based are plotted according to the equation $y = x^{1/2}$, a straight line for each parabola is obtained. Then, by squaring the straight line equation ($y = mx + b$) for each curve in Figure VI, the equations are obtained for the parabolas of Figure V. The values for m are taken from the straight lines of Figure VI.

Another feature is brought out by a study of Figure VI. Curves one and two, it is seen, are straight

lines which do not pass through the origin. Since this is true, therefore the parabolas of Figure V likewise do not pass through the origin, but instead have their vertex at y = -0.1. This can have but one meaning - that a certain period of irradiation is required at the beginning during which time no chemical reaction occurs. Such a period is known as an "Induction Period." The method employed in the study of the induction period, observed in this work, will be described before entering a discussion of the possible nature and cause of such a period of illumination preceding actual chemical reaction.

Reaction-mixtures of the same total volume containing the same quantity of formic acid but different amounts of ferric sulphate were subjected to irradiation. In all experiments, the current across the lamp was brought to a constant voltage (50 volts) and a constant intensity (3.6 - 3.8 amperes) before irradiation was begun. At definite five-minute intervals, small samples of the reaction mixtures were removed to test the presence of ferrous ions. The start of the photochemical reaction was indicated by a positive test for ferrous ions. The reagent (10% solution of potassium ferri-cyanide) employed for this test has a sensitivity of one part in one hundred thousand. The reaction mixtures irradiated and the results obtained are summarized in Table IX.

TABLE IX

Induction Period-Test for Ferrous Ions

Time of Irradiation	2.5 cc. 0.1762 M $Fe_2(SO_4)_3$ soln. 10 cc. 1.0M HCOOH 27.5 cc. Water	5 cc. $Fe_2(SO_4)_3$ soln. 10 cc. HCOOH 25 cc. Water	10 cc. $Fe_2(SO_4)_3$ soln. 10 cc. HCOOH 20 cc. Water
0 minutes	negative	negative	negative
5 "	"	"	"
10 "	positive	"	"
15 "	"	positive	very faint
20 "		positive	" "
25 "			positive

This experiment indicates that there is an induction period. Moreover, the time required when 5 cc. of 0.1762 molar ferric sulphate is irradiated, was found to be approximately 15 minutes. This agrees very well with the value read from the curves in Figure VI.

In discussing this phenomenon, it is appropriate at this time to give a brief historical sketch of induction periods observed by other workers in the field of photochemistry. Bunsen and Roscoe[62] studied the photochemical induction period of the hydrogen-chlorine reaction and concluded that it was dependent not only on the mode of preparation of the gases, but also on their former history,

being, for instance, greatly shortened by a previous illumination. This induction period has been thoroughly studied likewise by Burgess and Chapman[63] and Chapman and MacMahon[64]. These authors proved that the induction period is caused by impurities in the gases used, as well as by impurities on the walls of the containing vessel and in the absorbing liquid. The action of different impurities was found by these authors to be specific, for instance, oxidizing agents like nitric acid and hydrogen peroxide did not show it, but ammonia, nitrogen trichloride, chlorine dioxide, and some other substances, among which the organic compounds may especially be noted, increased the duration of the induction period enormously. All these substances are probably destroyed or eliminated from the gas phase on illumination, the full rate of hydrogen chloride formation being attained only after this purification has taken place.

Baly and Barker[65] came to a different conclusion concerning the nature of the induction period and suggested that it is an inherent property of the hydrogen-chlorine reaction.

Chapman and Gee[66] showed that oxygen causes an induction period in the chlorine-carbon monoxide reaction. Other impurities such as nitric oxide, ozone, and nitrogen chloride were active in this respect. Likewise, Benrath and Hertel[67] observed an induction

period in their study of the chlorination of saturated aliphatic compounds.

In connection with the induction period observed in the study of the photochemical oxidation of formic acid by ferric sulphate, it is interesting to note that while such a period exists for this reaction, there is none whatever for the photolysis of formic acid. This may readily be seen by a study of the curves in Figures V and VI. On the basis of the conclusion reached by the authors described above, it is conceivable that the induction period observed by the authors of this thesis may be caused by impurities present in the reaction mixtures involving ferric sulphate. Minute impurities in the ferric salt could explain the existence of an induction period for the photochemical oxidation of formic acid and not its photolysis. However, may it again be stated that extreme precautions were taken to eliminate impurities in so far as possible.

From another viewpoint and accepting the Bohr theory of atomic structure, it may be reasoned that such an induction period may be required, in the photochemical oxidation of formic acid to built up the energy of the system to the point where chemical reaction will occur. This subject offers an interesting problem for future research, which the authors of this paper believe to be necessary before definite conclusions can be reached.

F. Summary and Conclusions

(1) A modification of its mercuric chloride method for determining formic acid in the presence of small amounts of formaldehyde and in solutions containing ferrous or ferric sulphate has been developed.

(2) The four equations,

(a_1) $HCOOH \longrightarrow 2H^{\cdot} + CO_2$

(b_1) $HCOOH \longrightarrow CO^{\cdot} + HOH$

(a_2) $HCOOH + 2H^{\cdot} \longrightarrow HCHO + HOH$

(b_2) $HCOOH + CO^{\cdot} \longrightarrow HCHO + CO_2$

postulated by Allmand and Reeves to explain the mechanism of the photolysis of formic acid in aqueous solution, based upon analysis of the gases evolved, have been confirmed in another way - namely, by determining the quantity of carbon dioxide liberated and the amount of formic acid decomposed.

The experimentally determined molecular ratio of carbon dioxide evolved to formic acid decomposed 1.00 : 1.84, whereas the theoretical value is 1.00 : 2.00. The quantity of carbon dioxide evolved was found to be 97.1 per cent of theory, calculated on the assumption of the theory of Allmand and Reeves.

(3) The photochemical oxidation of formic acid by ferric sulphate, in conformity with the two following equations,

(a) $Fe_2(SO_4)_3 + HCOOH \longrightarrow 2FeSO_4 + H_2SO_4 + CO_2$

(b) $HCOOH \longrightarrow H_2 + CO_2$

is shown to be an entirely different type of decomposition than that by its photolysis. The experimentally determined molecular ratio of carbon dioxide evolved to the formic acid decomposed is 1.00 : 0.97, and agrees very well with the theoretical ratio of 1.00 : 1.00.

(4) The concurrent equations, postulated to represent the mechanism of the photochemical oxidation of formic acid by ferric sulphate, have been substantiated.

(5) A study of the change-time curves, which graphically represent the decompositions of formic acid by photolysis and by photochemical oxidation with ferric sulphate, show conclusively that the two types of decomposition are widely different.

Equations for the change-time curves are derived.

(6) Change-time curves, representing the photochemical oxidation of formic acid with ferric sulphate, do not pass through the origin. The increment on the x-axis, formed as a consequence, indicates that there is a period of irradiation preceding the start of the decomposition during which no chemical reaction takes place. The results, concerning this induction period, indicated by the graphs, have been checked by chemical measurements.

(7) It is likely that a further study of this induction period will show whether this is caused by traces of impurities or whether it represents a period which is required for building up the energy of the system before reaction can occur.

PHOTOCHEMICAL LITERATURE

A. Texts Studied

Photochemical Reactions in Liquids and Gases
Trans. of Faraday Society, 1925, 21, 484.

Photochemical Processes - Trans. of Faraday Society, 1931, 27, 357.

Chemical Action of Ultraviolet Rays - Ellis and Wells.

Photochemical Processes - G. B. Kistiakowsky.

Radiation in Chemistry - R. A. Morton

Photochimie - A. Berthoud.

Photo-processes in Gaseous and Liquid Systems - Griffith and McKeown.

Review of Photochem., Chemical Reviews - Vol. 3, pp. 198-225 by W.A. Noyes and Kassel.

Photochemie der Zukunst - W. G. Herz.

Die Chemischen Wirkungen des Lichts - F. Weigert.

Photochemistry - S. E. Sheppard

Radiation Theory of Chemical Kinetics & Photochemistry - Chem. Soc. - Annual Reports - Vol. XXII, 1925.

Lehrbuch der Photochemie - A. Benrath.

Photochemische Versuchstechnik - J. Plotnikow.

B. Bibliography

(1) H.S. Taylor - J. of Phys. Chem., Vol. 32, p.516, 1928.

(2) Plotnikow - Transactions of the Faraday Society, 1925, 21, 484.

(3) Bancroft - Ind.Eng.Chem., 1924, 16, 270.

(4) Bourgoin - Chem.Abst., 1923, 17, 2084.

(5) Fernau - J.C.S., 1923, 124 ii, 601.

(6) Smiths and Aten - Z.Electrochem., 1910, 16, 264.

(7) Plotnikow - Chem.Ztg. 1919, 43, 321-337;
Chem.Ztg. 1920, 44, 825.

(8) Nazarov - J.C.S., 1915, 108 ii, 754.

(9) Berthelot and Gaudechon - Compte.rend. 1912, 154, 1597;
J.C.S., 1912, 102 ii, 616.

(10) Leighton - J.C.S., 1913, 104 ii, 459.

(11) Gerretsen - Chem. Weekblad, 1916, 13, 220.

(12) Berthelot and Gaudechon - Compte.rend., 1911, 152, 376.

(13) Berthelot - Ann.Chim.Phys., 1900, VII, 19, 150.

(14) Suida - Monatshefte, 1912, 33, 1255.

(15) Kailan - J.C.S., 1920, 118 i, 538.

(16) Landau - J.C.S., 1912, 102 ii, 986.

(17) Berthelot and Gaudechon - Compte.rend., 1910, 150, 1327.

(18) Stobbe and Schmitt - Z.Wiss.Photochem., 1920, 20, 57.

(19) Henri and Ranc - Compt.rend., 1912, 154, 1261.

(20) Berthelot and Gaudechon - Compt.rend., 1913, 156, 233.

(21) Berthelot and Gaudechon - Compt.rend., 1913, 156, 68.

(22) Berthelot and Gaudechon - J.S.C. I, 1911, 30, 1086.

(23) Berthelot and Gaudechon - J.S.C. I, 1910, 29, 1081.

(24) A. Frank and E. Pollitzer - Chem.Abst., 1913, 7, 2543.

(25) Grossman - Z.Physik.Chem., 1924, 109, 305.

(26) Boeseken and Coehn - Chem.Abst., 1920, 14, 2786.

(27) Berthelot and Gaudechon - Compte.rend., 1912, 155, 401.

(28) Dorée and Dyer - Chem.Abst., 1917, 11, 1753.

(29) Berger - J.C.S., 1921, 119, 2070.

(30) Kailan - Monatshefte.Chem., 1913, 34, 1209.

(31) M. Landau - J.C.S., 1911, Ai, 515.

(32) Baudisch - Biochem.Zeit., 1920, 103, 59;
Chem.Abst., 1920, 14, 2776.

(33) Berthelot and Gaudechon - Compt.rend., 1910, 151, 478.

(34) Euler and Ryd - J.C.S., 1913, 104 ii, 544.

(35) Stoemer and Robert - Berichte., 1922, 55 B, 1030.

(36) Berthelot and Gaudechon - Compt.rend., 1914, 158, 1791

(37) W.A. Noyes and Kouperman - J.A.C.S., 1923, 45, 1398.

(38) Volmar - Compt.rend., 1925, 180, 1172.

(39) Volmar - Chem.Abst., 1924, 18, 1612.

(40) J.M.Eder - Wein.Akad.Ber., 82, p.606, 1880.

(41) Vries - Chem.Central., p.219, 1885.

(42) A. Benrath - J.C.S., 1905, 88, 730.

(43) Ross - J.A.C.S., 1906, 28, 790.

(44) A. Benrath - Z.Physik.Chem., 74, p.115, 1910.

(45) Euler and Ryd - J.C.S., 1913, 104 ii, 544.

(46) Euler and Ryd - Biochem.Zeitsch., 1913, 51, 97.

(47) Neuberg - Biochem.Zeitsch., 1912, 39, 158.

(48) Winther and Howe - Z.Wiss.Photochem., 1914, 14, 196.

(49) Bolin - Zeits.Physik.Chem., 1914, 87, 490.

(50) Volmar - Compte.rend., 1923, 176, 742-744.

(51) H.S.Fry and E.G.Gerwe - J.of Ind.and Eng.Chem., 1928, 20, 1392.

(52) H.S.Fry and R.D.Gerwe - M.A. Thesis, Univ. of Cincinnati, 1929.

(53) Berthelot and Gaudechon - Compte.rend., 1914, 158,1791.

(54) Allmand and Reeves - J.C.S., 1926, 129, 2852.

(55) Ramsperger and Porter - J.A.C.S., 1926, 48, 1267.

(56) Taylor and Bates - J.A.C.S., 1926, 48, 2840.

(57) Hatt - Z.Physik.Chem., 1918, 92, 513.

(58) Benrath - Z.Physik.Chem., 1910, 74, 115.

(59) E. Rupp and H. Schee - Biochem.Zeit., 1926, 172, 373.

(60) Association of Official Agricultural Chemists - p. 137.

(61) Levy and Pecoul - Comptes Rendus - 142 (1906), 162.

(62) Bunsen and Roscoe - Poggendorfs Annalen, 96 (1855); Poggendorfs Annalen, 108 (1859).

(63) Burgess and Chapman - J.C.S., 89, 1402 (1906).

(64) Chapman and MacMahon - J.C.S., 97, 845 (1909).

(65) Baly and Barker - J.C.S., 119, 653 (1921).

(66) Chapman and Gee - J.C.S., 99, 1726 (1911).

(67) Benrath and Hertel - Zeitschrift Wissenschaft Photochemie, 23, 30 (1924).