isolated products (mono- or diacetates or mixtures) which are entirely or very largely of the *cis*-configuration. It is considered most probable

that orthoacetate intermediates are involved in these transformations.

Reversible Photochemical Processes in Rigid Media: The Dissociation of Organic Molecules into Radicals and Ions

By Gilbert N. Lewis and David Lipkin

In previous papers[1] we have studied the phosphorescent state of dye molecules. This phosphorescent state returns to the initial state with light emission and is to be regarded as isomeric with the normal molecule. On the other hand, the present paper deals with the photo-dissociation of organic molecules into radicals, ions and electrons.

In a study of the absorption spectra of odd molecules we desired to investigate diphenylnitrogen, the free radical of tetraphenylhydrazine, but at any temperature at which the dissociation is appreciable the radical disappears as fast as it is formed, through processes of rearrangement or disproportionation. We therefore attempted to produce diphenylnitrogen by illuminating a solution of tetraphenylhydrazine in our EPA solvent (see experimental section) at low temperature.

The solution in a quartz tube was immersed in liquid air contained in a quartz Dewar. After a minute or two of exposure to the light from a high-pressure mercury arc the solution acquired a green color which we attributed to the formation of the diphenylnitrogen radical, although we shall see presently that other substances are also produced. The color persists for many days at the temperature of liquid air but rapidly disappears when the temperature is raised sufficiently to make the solvent fluid.[2] This rise of temperature for EPA is about 10°. That the disappearance of color is not primarily the effect of temperature but of the change in rigidity of the solvent is shown by the fact that most of the phenomena that we are going to describe are duplicated when the tetraphenylhydrazine is dissolved in glycerol or triethanolamine and illuminated at 190°K. and in a few cases similar phenomena have been obtained in glucose at room temperature.[3]

When the green solution is studied spectroscopically we find that, instead of one band, several prominent bands appear and we shall see that these belong to different substances, since their relative intensities vary greatly according to the way in which the solutions are prepared and treated. The absorption curves are shown in Fig. 1, in which the ordinates of each curve are proportional to the extinction coefficient, but with an arbitrary proportionality factor for each curve, since we have not yet determined the absolute concentration of any one of the substances.
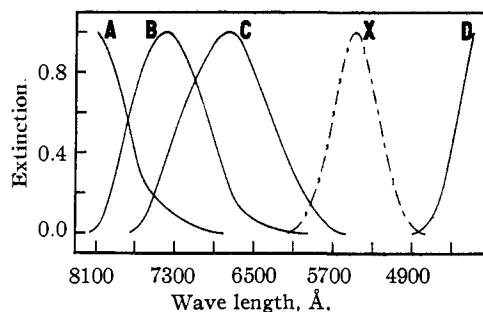

Fig. 1.—Absorption bands of tetraphenylhydrazine illuminated and measured in EPA at about 90°K. The ordinates for each curve are in arbitrary units.

In attempting to identify substances produced by illumination we are handicapped by

(1) (a) Lewis, Lipkin and Magel, This Journal, **63**, 3005 (1941); (b) Lewis, Magel and Lipkin, *ibid.*, **64**, 1774 (1942).

(2) The production of color by illumination in the cold and its disappearance on warming may be repeated many times with the same sample, although eventually a permanent yellow color appears. Quantitative experiments show that when the initial illumination is carried to the point where all of the tetraphenylhydrazine is gone, more than 90% of it is regenerated on warming. From the fact that diphenylnitrogen is one of the chief products of the photo-dissociation and that this returns to tetraphenylhydrazine, even at very low temperatures, we have recently drawn certain conclusions regarding the heat of dissociation of the latter compound [Lewis and Lipkin, This Journal, **63**, 3232 (1941)].

(3) The only antecedents that we have been able to find in the literature to the phenomena that are to be here described are in the inorganic field the coloration of glasses after long exposure to light and in the organic field the observations of Wieland [*Ann.*, **381**, 216 (1911)], who exposed crystalline substances such as the tetraaryl-hydrazines to electron bombardment at the temperature of liquid air. He obtained strong coloration which he attributed to free radicals. The color disappeared within a few minutes after the bombardment ceased.

being unable to study any of the physical properties of the new substances except their reactions with photons (absorption and luminescence).[4] On the other hand, we have the great advantage of working with isolated molecules. At the small concentrations that we use, 10^{-4} M or less, the individual molecules are on the average over 100 Å. apart and when the solution is cooled to rigidity no appreciable diffusion can occur, and therefore no bimolecular reactions. Except in cases where the solute is polymerized before the state of rigidity is attained, the simple molecule and the group of solvent molecules in its immediate neighborhood alone can participate in the photochemical process or in the reactions which occur after illumination. This restriction of all processes in the rigid solvent to the zone of a single molecule limits the number of possible structures that may be assigned to the photochemical products.

In order to investigate the several absorption bands obtained by illuminating tetraphenylhydrazine the frequency of the activating light may be varied, the effect of further illumination by light of various frequencies may be observed, and if the temperature is gradually raised we may see which substances first disappear, and whether the disappearance is accompanied by an increase in any of the other bands. Finally, we may activate with polarized light and study the molecular orientation of the products. In addition to these experiments on tetraphenylhydrazine itself we may illuminate other substances containing the diphenylnitrogen group and find whether we can reproduce any of the bands already observed.
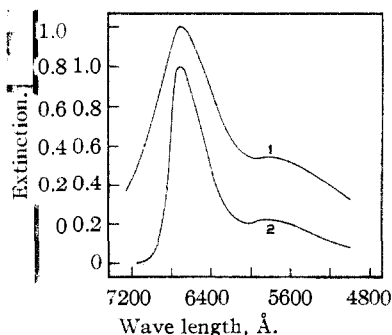

Fig. 2.—Absorption of $(p\text{-}CH_3C_6H_4)_3N^+$: Curve 1, Granick and Michaelis by chemical oxidation; Curve 2, by photo-oxidation in EPA at about 90°K.

We shall find three types of photochemical reaction. The first is the one already mentioned, namely, splitting into two uncharged radicals, and this for brevity will be called *photo-dissociation*. Second, a molecule may be split by light into a positive and a negative ion. This *photo-ionization* is also observed under ordinary conditions in such substances as the leucocyanides of crystal violet and malachite green.[5] Since these positive ions behave as secondary acids[6] the recombination of the ions in the dark is observably slow at room temperature. Third, the illuminated molecule may merely eject an electron. To distinguish this from the preceding type of process we shall call it *photo-oxidation*, and indeed the simplest of all oxidation processes is the loss of an electron. Since this photo-oxidation is a new and somewhat surprising phenomenon we shall first present the evidence for its existence.

Photo-oxidation by the Loss of an Electron

Upon illuminating a variety of substances in rigid media it soon became apparent that one of the commonest photochemical processes is the mere loss of an electron by the activated molecule. When triphenylamine was illuminated at liquid air temperature in EPA a blue color was obtained. The absorption curve showed a maximum at 6560 Å. and a shoulder in the neighborhood of 5700 Å. The curve was so similar to a curve obtained by Granick and Michaelis[7] (Curve 1, Fig. 2) for the ion of tri-p-tolylamine, $(p\text{-}CH_3\text{-}C_6H_4)_3N^+$, produced by chemical oxidation of tri-p-tolylamine, that it seemed very probable that our blue substance was $(C_6H_5)_3N^+$. This *odd* ion is so unstable because of the lability of the para hydrogens that it cannot readily be obtained by chemical oxidation. We were, therefore, very grateful to Drs. Granick and Michaelis for sending us a sample of the tri-p-tolylamine used in their investigation. When this was illuminated in the rigid solvent we obtained the substance whose absorption is given in Curve 2 of Fig. 2. There can be no question that chemical oxidation at room temperature and photo-oxidation at liquid air temperature have given the same substance, namely, the positive ion left when one electron has been removed. In order to produce photo-oxidation of triphenylamine and tri-

(4) We have not attempted to study the magnetic susceptibility of our solutions. Such an investigation, while difficult, would be profitable.

(5) This phenomenon has recently been carefully studied by Harris, Kaminsky and Simard [THIS JOURNAL, **57**, 1151 (1935)].

(6) Lewis, *J. Franklin Institute*, **226**, 2093 (1938); Lewis and Seaborg, THIS JOURNAL, **61**, 1886 (1939).

(7) Granick and Michaelis, *ibid.*, **62**, 2241–2242 (1940).

p-tolylamine it is necessary to illuminate with the full mercury arc through quartz, but even so it is surprising to find the energy sufficient to expel an electron according to the process

$$Ar_3N \longrightarrow Ar_3N^+ + e^-$$
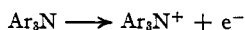
As to what becomes of the electron we can only speculate. It presumably becomes attached to a solvent molecule,[8] or to a group of molecules, or even to some unique point in the solvent determined by its rigid structure. The electron must lie in a potential hole which is deep enough so that the large electrostatic field of the ion is unable to dislodge it. The color persists at liquid air temperature for several days, but at only slightly higher temperatures the color disappears. Then presumably the electron has returned to the ion.

Another case where we may compare our results with those of Michaelis and his collaborators is that of Wurster's blue, $(CH_3)_2N\langle\bigcirc\rangle N(CH_3)_2 \Big]^+$ They prepared this odd ion by chemical oxidation, and their absorption spectrum[9] obtained at room temperature in partly aqueous solutions is given in Curve 1, Fig. 3. We dissolved the colorless base of Wurster's blue in EPA and illuminated in liquid air. The absorption spectrum was then measured above rapidly boiling liquid air.[10] The results are given in Curve 2, Fig. 3. In spite of the difference in solvent and in temperature the agreement of the two curves

is remarkable, and definitely proves the ejection of an electron by light.[11]

Owing to the complete elimination of bimolecular reactions in a rigid solvent we may by this method of photo-oxidation obtain and study numerous odd ions which, under ordinary circumstances, would engage in further reactions almost as soon as formed. The triphenylamine ion is an example. As further illustrations of odd ions produced by light through the ejection of electrons, we give in Fig. 4 the very

Fig. 4.—Absorption of tetramethylbenzidine ion produced by photo-oxidation in EPA at about 90°K. The sample was not specially purified.

complex spectrum of tetramethylbenzidine ion, $(CH_3)_2N\langle\bigcirc\rangle\langle\bigcirc\rangle N(CH_3)_2 \Big]^+$, and in Fig. 5 the spectrum of methyldiphenylamine ion, $(C_6H_5)_2$-NCH_3^+. The spectra of several other odd ions will be given in later sections.
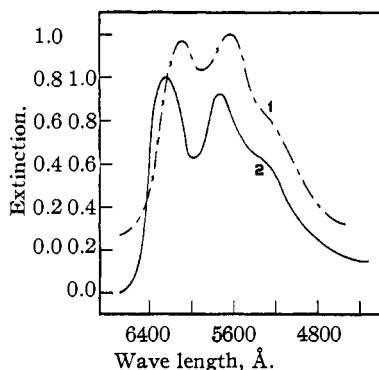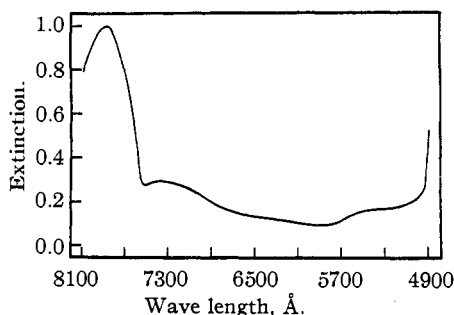

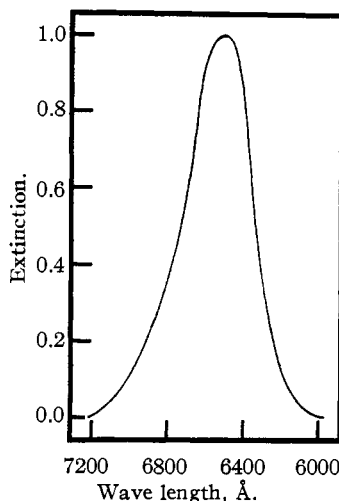Fig. 3.—Absorption of Wurster's blue: Curve 1, Michaelis, Schubert and Granick by chemical oxidation; Curve 2, by photo-oxidation in EPA at about 90°K.

Fig. 5.—Absorption of methyldiphenylamine ion produced by photo-oxidation in EPA at about 90°K.

(8) In a mixture of equal volumes of ether and isopentane the same results were obtained as in EPA. On the other hand, in a solvent of mixed hydrocarbons (3 vols. of isopentane to 1 vol. of methylcyclohexane) little or no blue color was produced. Whether, however, this failure was due to lack of oxygen atoms in the solvent or to a lesser rigidity of the hydrocarbon solvent, we have not as yet ascertained.

(9) Michaelis, Schubert and Granick, THIS JOURNAL, 61, 198 (1939).

(10) Lewis, Magel and Lipkin, *ibid.*, 62, 2973 (1940).

(11) When the ion of Wurster's blue was produced in a solvent containing air a slight blue color remained after warming. If this is due to the permanent capture of electrons by the oxygen molecules, a study of the amount of residual color as a function of the oxygen concentration might indicate how far the electron is ejected.

Further cases of presumable photo-oxidation were found in a cursory examination of the following substances which gave the colors noted, the color disappearing when the solvent became liquid. These experiments should be repeated with more carefully purified materials.

Substance	Color
Hydroquinone	Orange-yellow
α-Naphthol	Reddish-orange
p-Hydroxydiphenyl	Orange
Thiophenol	Yellow
o-Thiocresol	Yellow
Thio-β-naphthol	Orange-red
p-Hydroxythiophenol	Orange

Photo-dissociation into Free Radicals

In order to make sure that dissociation into free radicals does occur under the conditions of our experiments, we slowly cooled in a sealed quartz tube a solution of triphenylmethyl in EPA. At about −50° it was so completely converted into hexaphenylethane that the free radical could no longer be detected spectroscopically. It was then placed in a quartz Dewar containing liquid air and illuminated by the mercury arc. After ten minutes of exposure the solution showed the sharp and unmistakable absorption bands of triphenylmethyl. The slow formation of the free radical, in spite of the small energy of dissociation, may indicate that the main absorption of hexaphenylethane comes at higher frequencies than are afforded by the mercury arc.
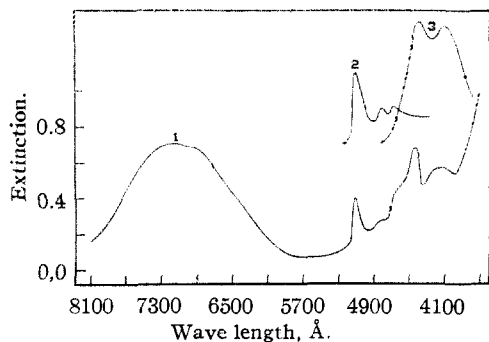

Fig. 6.—Curve 1 obtained by illuminating triphenylmethyldiphenylamine in EPA at about 90°K.: Curves 2 and 3 (with a higher base line), absorption curves of $(C_6H_5)_3C$ and $(C_6H_5)_3C^+$, respectively.

The next substance investigated was diphenyl disulfide. A solution of this substance becomes yellow on heating and nearly colorless on recooling. According to Schönberg[12] it does not obey Beer's law, so that it has been concluded
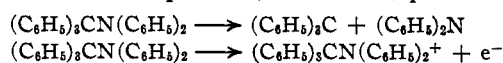
(12) Schönberg, Trans. Faraday Soc., 30, 17 (1934).

that there is partial dissociation to give the free radical C_6H_5S. We have studied photographically the absorption of diphenyl disulfide in ethyl benzoate at 210°, with 1- and 5-cm. cells, and have found entirely similar but fainter absorption in ethanol with a 61-cm. cell at room temperature. While we have not yet studied the plates photometrically, the absorption band is a broad one beginning in the visible region and still rising at 3900 Å. The disulfide was next dissolved in EPA and illuminated at liquid air temperature. The resulting yellow solution showed, as was expected, the same band of C_6H_5S, but there is also a strong band with a maximum at 4600 Å. Obviously, another process besides photo-dissociation occurs and we believe that it is another case of photo-oxidation and that the new band is due to $C_6H_5SSC_6H_5^+$. As in all our experiments, except when there is an explicit statement to the contrary, the color disappeared as the solvent was warmed to fluidity. Therefore both processes are reversed at very low temperature, showing that, as in the case of diphenylnitrogen, there is no appreciable heat of activation for the dimerization of the phenylsulfur radical.

The next substance studied (EPA, liquid air) was triphenylmethyldiphenylamine, $(C_6H_5)_3CN-(C_6H_5)_2$. Here we expected to find photo-dissociation into the two radicals triphenylmethyl and diphenylnitrogen, but the process proved to be more complicated, as may be seen from the absorption spectrum of Fig. 6. In addition to Curve 1, which shows the result of this experiment, we give in Curve 2 the absorption of triphenylmethyl according to our own measurements (90°K., EPA), which agree very closely with those of Anderson,[13] and in Curve 3 the absorption of $(C_6H_5)_3C^+$ as obtained by Anderson. It is evident that both of these substances are present.[14] On the other hand, the ions $(C_6H_5)_3C^-$ for which Anderson obtained an absorption maximum at 4800 Å., and $(C_6H_5)_2N^-$ whose absorption we give in Fig. 8, are not present in appreciable amount. There is, therefore, no evidence of photo-ionization into positive and negative ions. On the other hand it appears that we must write at least two

(13) Anderson, THIS JOURNAL, 57, 1673 (1935).

(14) While the parent substance is not sensitive to air at room temperature and below, we found that the absorption band of triphenylmethyl did not appear in the low temperature illumination unless the solution had been carefully freed from oxygen. Since in the rigid solvent it seems hardly possible for the oxygen to diffuse to the triphenylmethyl that is formed, we seem forced to the conclusion that the oxygen molecule is already there; in other words, that the parent substance must form some loose complex with the oxygen on cooling.

photochemical equations, which are, presumably

$$(C_6H_5)_3CN(C_6H_5)_2 \longrightarrow (C_6H_5)_3C + (C_6H_5)_2N$$
$$(C_6H_5)_3CN(C_6H_5)_2 \longrightarrow (C_6H_5)_3CN(C_6H_5)_2^+ + e^-$$

the last substance then breaking into $(C_6H_5)_3C^+$ and $(C_6H_5)_2N$, and possibly into $(C_6H_5)_3C$ and $(C_6H_5)_2N^+$. Obviously our hope of obtaining in this way the pure spectrum of $(C_6H_5)_2N$ was a vain one and the left-hand portion of our curve is a superposition of the curves for $(C_6H_5)_2N$, $(C_6H_5)_2N^+$, and perhaps $(C_6H_5)_3CN(C_6H_5)_2^+$.

Photochemical Reactions of Other Compounds Containing the Diphenylnitrogen Group

With the object of identifying the bands obtained in the illumination of tetraphenylhydrazine we have treated by a similar procedure several substances in which the diphenylnitrogen group occurs.

Nitrosodiphenylamine, $(C_6H_5)_2NNO$, **and Diphenylhydrazine,** $(C_6H_5)_2NNH_2$.—The illumination of these two substances in EPA at liquid air temperatures gave green solutions of which the absorption spectra are given, respectively, in Curves 1 and 2 of Fig. 7. While we shall later discuss these curves briefly it may be noted now that their appearance is not inconsistent with the assumption that we have produced in varying amounts the two substances responsible for the B and C bands of illuminated tetraphenylhydrazine.
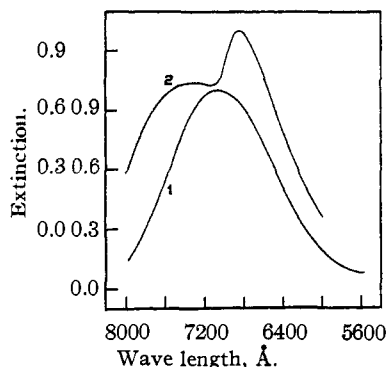
Fig. 7.—Absorption after illumination of (1) $(C_6H_5)_2NNO$ and (2) $(C_6H_5)_2NNH_2$.

Lithium Diphenylamide, $(C_6H_5)_2NLi$.—In order to study the diphenylamide ion it was necessary to use a solvent containing no alcohol, since the ion is an even stronger base than alcoholate ion. The lithium diphenylamide was found to be sufficiently soluble for our purpose in a mixture of two parts of isopentane and one part of ether. The absorption curves at this temperature before and after illumination are given in Curves 1 and

2 of Fig. 8. It appears that the second curve is identical with that of the B band of tetraphenylhydrazine.
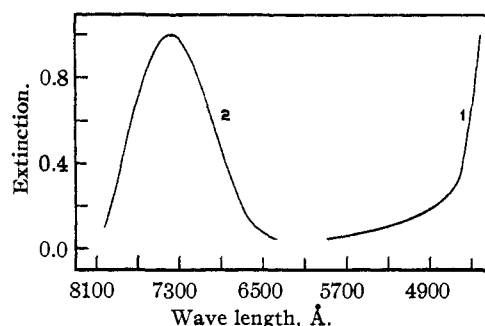
Fig. 8.—Absorption of a solution of lithium diphenylamide in ether and isopentane at about 90°K.: (1) before illumination, (2) after illumination.

Diphenylamine, $(C_6H_5)_2NH$.—While the illumination of triphenylamine and methyldiphenylamine gave simple photo-oxidation, the phenomena attending the illumination of diphenylamine proved to be of such complexity as to require a thorough investigation. When this substance in a rigid solvent is illuminated by the mercury arc, through quartz, it shows by transmitted light a purple color which takes an appreciable time, not more than a second, to rise to full intensity and disappears in about the same time after the illumination has ceased. The absorption spectrum while the sample is subjected to cross-illumination by the mercury arc is shown in Curve 3, Fig. 9. Since the half-life of the purple substance seems to correspond to that of the blue fluorescence of diphenylamine, it is probable that this absorption curve belongs to a phosphorescent state, such as we have previously studied in the case of fluorescein[1a] and of crystal violet.[1b]
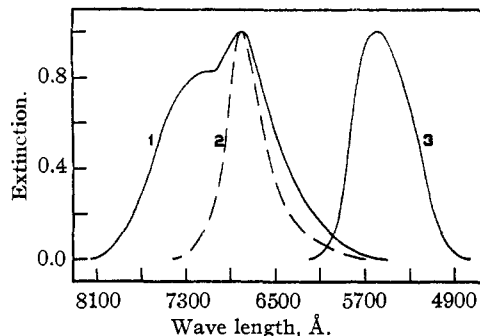
Fig. 9.—In EPA at about 90°K.: Curve 1, an example of the absorption curve obtained after prolonged illumination of diphenylamine; Curve 2, after brief illumination; Curve 3, absorption of the phosphorescent state of diphenylamine obtained while it is being illuminated.

As the illumination is prolonged the purple color disappears and is replaced by a green color which persists indefinitely after illumination has ceased. Ordinarily the absorption curve of the solution so obtained is not simple. One such curve is reproduced in Curve 1 of Fig. 9. If, however, we use only a brief illumination we obtain Curve 2 of Fig. 9. This so strongly resembles the curve of the positive ion of methyldiphenyl-amine (Fig. 5) that we have little hesitation in ascribing it to the corresponding ion, $(C_6H_5)_2NH^+$.

Numerous curves obtained on longer illumination, the analysis of which we shall not describe in detail, indicated the presence, in addition to $(C_6H_5)_2NH^+$, of the two substances responsible for the B and C bands of tetraphenylhydrazine. More recent experiments of Mr. J. Bigeleisen have shown that in the absence of air the C band does not appear, and the only bands are that of $(C_6H_5)_2NH^+$ and the B band of tetraphenylhydrazine, in amount depending on the length of illumination. Both of these bands disappear gradually as the temperature is raised, that of the $(C_6H_5)_2NH^+$ going more rapidly.

Interpretation of the Several Bands Obtained with Tetraphenylhydrazine

The X and D Bands.—Before considering the three main bands of Fig. 1 we shall say what we can of the elusive X band which sometimes is nearly one-third as strong as the B band, but sometimes does not appear at all. It never appeared when the illumination was by the full mercury arc through quartz. It appeared at its strongest when the illumination was with light lying between 3600 and 3800 Å. The difference proved to be due to the fact that the X substance is destroyed by all ultraviolet light as well as by the visible, in the range of absorption. Only when the frequency is in the neighborhood of 3700 Å. is the rate of its formation large compared with the rate of its destruction. On the other hand, the X substance is not very sensitive to temperature and persisted on warming as long as any color remained in the solution. Suspecting that the X band might be due to an impurity, a new preparation of tetraphenylhydrazine was made which gave under similar conditions the same curves as the preceding preparation but the X band was never more than one-half as intense. Until further preparations are tested we must doubt that the X band belongs to tetraphenylhydrazine.

The D band lay nearly outside the scope of our measuring apparatus and has therefore been little studied. It presumably does not represent an additional substance, but is part of a second band system of substance B, or substance C, or both.

The A Band.—This band, lying altogether in the infrared and with a maximum beyond the limits of our experiments, probably at about 8200 Å., might not have been discovered except for the short life of the A substance. We found that in the course of our absorption measurements over boiling liquid air that the absorption at the lowest frequencies fell off rapidly with time. It seemed, therefore, that the A absorption might readily be obtained by subtracting the curve obtained after the disappearance of A. The problem, however, was not so simple as this, for sometimes, as the A absorption diminished, that in the B and C regions substantially increased. It was finally found that A disappears by two processes, the first of which produces no change in the amounts of B and C, and the second of which produces both B and C. Fortunately at low temperatures (ca. 90°K.) the first process occurs almost alone and under these circumstances our method of subtracting the curves obtained before and after standing, enable us to obtain the curve for the A band given in Fig. 1.

We are going to identify the A substance with the positive ion of tetraphenylhydrazine, $(C_6H_5)_2NN(C_6H_5)_2^+$. This is the one band that does not appear when other compounds containing the diphenylnitrogen group are illuminated, and its absorption maximum in the infrared is about that which would be expected for an odd ion possessing such great possibilities of resonance.[15]

The B and C Bands.—We have seen that at higher temperatures the disappearance of A is accompanied by the production of B and C. By studying the light absorption at 8100 Å. and its change with time we have followed the kinetics of this reaction at about 90°K. The process proved to be strictly unimolecular with a half-life of twenty minutes. Concurrently the change of absorption in other parts of the spectrum were followed and it was seen that the B and C bands increased as they would if B and C were being

(15) In arriving at this conclusion it has been necessary to disregard the work of Weitz and Schwechten [*Ber.*, **60**, 1203 (1927)] and of Weitz and Müller [*ibid.*, **68**, 2306 (1935)] who by a variety of methods obtained violet substances which they believed to be the positive ions of tetraarylhydrazines. Some experiments similar to theirs but leading to a quite different interpretation will be discussed in the immediately following paper by Lewis and Bigeleisen.

produced from A. It is to be assumed that this thermal reaction is

$$(C_6H_5)_2NN(C_6H_5)_2{}^+ \longrightarrow (C_6H_5)_2N + (C_6H_5)_2N^+$$
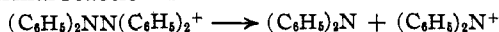
These observations, together with the appearance of the B and C bands in illumination of other compounds containing the diphenylnitrogen group, lead us to identify these bands with the substances $(C_6H_5)_2N$ and $(C_6H_5)_2N^+$. It remains to decide which substance should be assigned to which curve. The first evidence came from the observation that upon brief illumination only the A and B bands appeared. The two most likely reactions in a primary illumination, that is, an illumination which is not long enough to excite further the first products of illumination, are

$$(C_6H_5)_2NN(C_6H_5)_2 \longrightarrow (C_6H_5)_2NN(C_6H_5)_2{}^+ + e^-$$
$$(C_6H_5)_2NN(C_6H_5)_2 \longrightarrow 2(C_6H_5)_2N$$
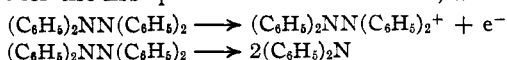
We believe that these two photochemical reactions occur in about equal amount and conclude that the B band is due to $(C_6H_5)_2N$ and therefore that the C band is due to $(C_6H_5)_2N^+$. By illuminating briefly and allowing the sample to stand at not too high a temperature, we were able to obtain the very satisfactory B band given in Fig. 1. On the other hand, the C band, which was obtained by a rough analysis of various compound curves, cannot be considered very accurate.

The assignment of the B and C bands enabled us to interpret satisfactorily the results obtained with other substances containing diphenylnitrogen. The illumination of triphenylmethyldiphenylamine gave $(C_6H_5)_2N$, $(C_6H_5)_3C$, $(C_6H_5)_2N^+$ and $(C_6H_5)_3C^+$, all of which can be recognized in Fig. 6. The illumination of $(C_6H_5)_2NNH_2$ seems from Fig. 7 to give largely photo-ionization according to the reaction

$$(C_6H_5)_2NNH_2 \longrightarrow (C_6H_5)_2N^+ + NH_2{}^-$$
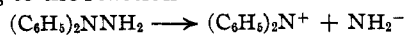
The illumination of $(C_6H_5)_2NNO$ apparently gives both $(C_6H_5)_2N$ and $(C_6H_5)_2N^+$, but we should like to study this case more carefully before attempting to write the photochemical reactions.

The case of diphenylamine is interesting. We have seen that the primary illumination produces only photo-oxidation to give $(C_6H_5)_2NH^+$, but then on further illumination there is a second reaction which must be written

$$(C_6H_5)_2NH^+ \longrightarrow (C_6H_5)_2N + H^+$$
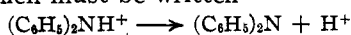
and thus the B band is obtained.[16]

(16) It is to be presumed that the proton attaches itself to the basic oxygen of the ether or alcohol of the solvent. It is probable also that in some of our other reactions the neighboring solvent molecules may take part to the extent of forming loose addition compounds presumably without causing appreciable change in the absorption spectra.

Perhaps the least ambiguous evidence for our assignment of the B band to the diphenylnitrogen radical is obtained in the experiment with diphenylamide ion. It seemed unlikely in this case that the primary illumination would cause anything except simple photo-oxidation
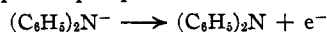
$$(C_6H_5)_2N^- \longrightarrow (C_6H_5)_2N + e^-$$

and the appearance in Fig. 8 of the pure B band seems almost by itself sufficient to identify this band with $(C_6H_5)_2N$.

Illumination by Polarized Light and the Production of Permanent Dichroism in Homogeneous Media.—We planned to resolve the complicated band system obtained by the illumination of tetraphenylhydrazine by using polarized light, and thus obtain an orientation of the resulting molecules which would be permanent as long as the medium remained rigid, but otherwise would be entirely similar to the orientation in the phosphorescent state that we previously studied.[1a] We have not been able to carry out this program but have nevertheless, with one or two simpler substances, shown that the method is practical. In these cases colored solutions were obtained which when studied with polarized light showed a notable variation of the absorption with the direction of polarization.

Experimental

In several cases (hexaphenylethane and the several di- and triarylamines) light between 2500 and 3000 Å. proved to be necessary for rapid photochemical action, and direct light from the high-pressure mercury arc was employed. In other cases the light passed first through a large quartz cell containing aqueous copper sulfate in order to use a high intensity of light without overheating the samples. Such overheating may easily occur even when the samples are immersed in liquid air. Various color filters were occasionally used to give selected spectral regions. The cells of quartz, or of "Pyrex" glass when permissible, were ordinarily about 1 cm. in thickness. Sometimes the color obtained was nearly uniform throughout the cell, but sometimes it all appeared near the face, in which case both faces were illuminated in turn. The depth of penetration of color depends upon the concentration and also upon the position and intensities of the ultraviolet absorption bands of the initial and final substances. Occasionally, a very dilute solution was illuminated in a tube 10 cm. long and 3 cm. in diameter, the illumination being across, and the absorption measurements along, the tube. The absorption measurements were made by methods that we have previously described.[1a]

Materials.—Tetraphenylhydrazine was prepared by the oxidation of diphenylamine with potassium permanganate, as described by Gattermann and Wieland.[17] It was not

(17) Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Co., New York, N. Y., 1934.

easy to determine the purity of the product since the substance decomposes before melting. We have mentioned that the X band shown in Fig. 1 may be due to impurity.

The hexaphenylethane was prepared *in vacuo* by the action of silver amalgam on triphenylchloromethane by a method that we shall describe more fully in another place. The triphenylmethyldiphenylamine was also made *in vacuo* by the method of Wieland.[18] Tetraphenylhydrazine was added to a solution of hexaphenylethane in toluene and heated two hours at 100°. When once formed the product can be filtered and recrystallized in the air, although after some months it deteriorates on standing in air.

Lithium diphenylamide was prepared as follows. A small amount of lithium and a slight excess of diphenylamine were placed in a tube on the vacuum line and ethylamine was distilled into the tube. After the completion of the reaction the ethylamine was pumped off and the mixture of ether and isopentane was distilled in. The tube was then sealed off. *unsym*-Diphenylhydrazine was prepared from the hydrochloride by adding alkali and shaking out with benzene. It was purified by vacuum distillation, as were also diphenylamine and methyldiphenylamine. Diphenyl disulfide was purified by recrystallizing from toluene at −80°.

Rigid Solvents.—At room temperature transparent glasses of boric acid or of glucose may be used. At −60 to −80° glycerol, triethanolamine, sulfuric and phosphoric acids make good rigid solvents. At the temperature of liquid air most supercooled liquids crack. Others have too little solvent power. We have found[10] that for most purposes the best solvent is a mixture of 5 parts of ether, 5 parts of isopentane,[19] and 2 parts of alcohol by volume. This we designate as EPA or more explicitly $E_5P_5A_2$. We have used higher alcoholic contents up to EPA_4, but the chance of the solvent cracking in the midst of an experiment increases with the alcoholic content. In the experiment

with lithium diphenylamide the solvent was EP_2. In other cases triethylamine may replace the alcohol in EPA. If a rigid solvent containing only hydrocarbons is desired, a mixture of 3 parts isopentane and 1 part methylcyclohexane is useful.

Summary

When tetraphenylhydrazine in a rigid solvent is illuminated by ultraviolet light, the solution becomes colored and shows three main absorption bands, each of which is shown to be due to a separate substance. In order to identify these substances and to find what types of photochemical reaction are possible under these circumstances, various substances have been similarly studied. It is found that a molecule may be dissociated by light into two radicals, into positive and negative ions, and into a positive ion and an electron. In two cases the last type of dissociation, which may be called photo-oxidation, gives substances identical with those obtained by Michaelis and associates by chemical oxidation. From the illumination of several substances containing the diphenylnitrogen group it has been possible to find the absorption bands of $(C_6H_5)_2N$ and $(C_6H_5)_2N^+$. These are two of the main substances produced in the illumination of tetraphenylhydrazine. The third is $(C_6H_5)_2NN(C_6H_5)_2^+$, which disappears by two processes: one is the return of the electron, the other is dissociation into $(C_6H_5)_2N$ and $(C_6H_5)_2N^+$. The latter process is shown to be unimolecular.

(18) Wieland, *Ann.*, **381**, 214 (1911).

(19) We are indebted to the Shell Development Company for a liberal donation of isopentane of high purity.

The Initial Step in the Action of Acids on Tetraarylhydrazines

BY GILBERT N. LEWIS AND JACOB BIGELEISEN

Wieland[1] observed that tetraarylhydrazines react with acids to give colored substances which according to circumstances are green, violet or blue. In fact, a single preparation passes, sometimes rapidly, through a succession of color changes. If the solution has not aged much, Wieland showed that neutralization by alkali restores a large part of the original hydrazine and therefore concluded that the acid produces a mere addition complex without splitting the hydrazine. However, it has not been found possible to suggest any such addition compound that would have any of the observed colors. Weitz and others[2] have assumed a more or less reversible reaction which in the case of tetraphenylhydrazine may be written

$$3(C_6H_5)_2NN(C_6H_5)_2 + 2H^+ = 2(C_6H_5)_2NH + 2(C_6H_5)_2NN(C_6H_5)_2^+ \quad (1)$$
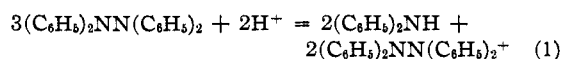
It is to such odd ions as the one appearing in this equation that Weitz ascribes the violet color obtained by the action either of acids or of oxi-

(1) Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, 1913.

(2) Weitz and Schwechten, *Ber.*, **60**, 1203 (1927); Weitz and Müller, **68**, 2306 (1935).