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

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

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

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.

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 sug-

gest 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

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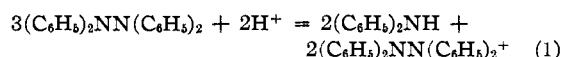
It is to such odd ions as the one appearing in this equation that Weitz ascribes the violet color obtained by the action either of acids or of oxi-

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

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

dizing agents on tetraarylhydrazines. However, it has been shown in the adjoining paper of Lewis and Lipkin[3] that this ion, which is produced from tetraphenylhydrazine by the loss of an electron, is certainly not violet, for its chief absorption is in the infra-red. In fact, the violet color as described by Wieland and by Weitz must be the resultant of a complicated series of reactions; we have never observed the violet color in non-hydroxylic solvents in the absence of air.

Another objection to regarding equation (1) as the primary step in the process is that such a reaction would presumably have a considerable heat of activation, but we find that the production of color upon acidifying tetraphenylhydrazine is extremely rapid nearly down to the temperature of liquid air.[4] It is possible that on the way to some of the end-products that have been identified by Wieland, reaction (1) may play a part, but here we are concerned only in finding what the first step in the reaction is.

Considering the various possible initial reactions the only one that seems reasonable is the one that assumes that tetraphenylhydrazine is in rapid equilibrium with a small amount of its two ions according to the equation

$$(C_6H_5)_2NN(C_6H_5)_2 \rightleftharpoons (C_6H_5)_2N^+ + (C_6H_5)_2N^- \quad (2)$$

and that upon addition of acid the negative ion is removed[5] allowing the positive ion to accumulate to such extent as to show its green color. We should expect, therefore, to obtain initially, in the absorption spectrum, the band designated as the "C" band in the preceding paper.

Our first experiments were made between 200°K. and room temperature. Solutions of tetraphenylhydrazine in various solvents such as acetone, ether, isopropyl chloride, β-n-amylene, and several mixtures of these, sometimes including isopentane, were exhausted on the vacuum

(3) Lewis and Lipkin, THIS JOURNAL, 64, 2801 (1942).

(4) As far as we can judge the reaction may still be instantaneous at temperatures below that of liquid air, but at these low temperatures even the most fluid solvents, such as isopentane, become very viscous and the reaction time is the time required for mixing.

(5) We shall not attempt to decide whether hydrogen ion adding to $(C_6H_5)_2N^-$ forms diphenylamine immediately or whether possibly the nitrogen acts as a secondary base, and therefore the hydrogen ion attaches itself at a para position in one of the rings. When dry hydrogen chloride is added to a solution of tetraphenylhydrazine in isopentane at low temperatures a typical green solution is formed, but further addition of acid produces a red precipitate. This phenomenon, which is evidently due in some way to the addition of a second hydrogen ion or acid molecule, may be avoided by buffering the solvent with any base such as ether, acetone or alcohol to keep down the acid strength. The use of such buffers in solvents which are not sources of hydrogen ion will be obvious to those familiar with the theory of generalized acids and bases (see Lewis, J. Franklin Institute, 226, 293 (1938)).

bench after cooling with liquid air, and dry hydrogen chloride gas was allowed to enter. Then either the containing tubes were sealed off or the solution was gradually warmed and stirred by a simple magnetic stirrer. All the solutions showed apparently the same green color. However, on spectrophotometric examination the absorption curves varied greatly from sample to sample, depending upon the solvents and the temperature attained before making the measurements; none showed the expected pronounced maximum at the position of the "C" band (about 6800 Å.). It is evident that even under the conditions of these experiments numerous colored substances have been produced.

The first indication of the "C" band appeared in a solution in ether, isopentane and isopropyl chloride (1,1,2 by volume). After freezing the solution in liquid air, passing in hydrogen chloride (in moles about equal to the amount of tetraphenylhydrazine used) and warming to about 160°K., the solution was stirred, and once again cooled. The absorption measurements were made just above rapidly boiling liquid air. The experiment was unsatisfactory because of the clouding of the solvent, but there appeared to be definite evidence of an absorption maximum in the neighborhood of the "C" band.

A more conclusive experiment was then performed using our EPA solvent, ether, isopentane and ethanol (5,5,2 by volume). The procedure was that just described except that the solution was treated with hydrogen chloride at about 130° K., was stirred about half a minute and then cooled to 90°K., where the absorption measurements were made. The absorption curve obtained is shown as curve 1 in Fig. 1. In the same figure curve 2 taken from the preceding paper of Lewis and Lipkin[3] shows roughly the "C" band attributed to $(C_6H_5)_2N^+$. There seems little doubt that the positive ion of diphenylnitrogen is one of the first substances produced in the action of an acid on tetraphenylhydrazine. That it is this ion, and not the accompanying substance with an absorption chiefly in the infra-red, that is actually the first colored product of the reaction, is shown by the fact that when the solution is warmed to a little higher temperature the "C" band disappears and only the infra-red band remains.[6]

(6) It seems likely that the substance responsible for the infra-red band is formed from the positive diphenyl nitrogen ion by a disproportionation involving the para hydrogen. Our experiments, therefore, should be repeated with tetra-p-tolylhydrazine so as to exclude this type of side-reaction.
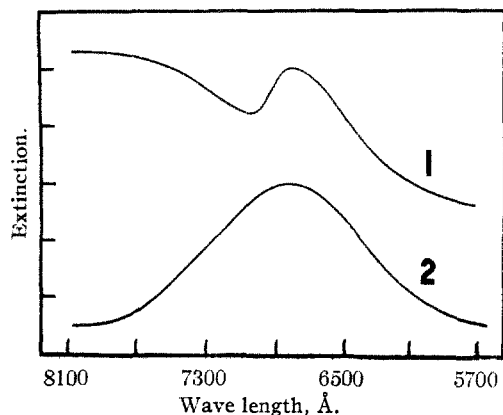
Fig. 1.—1, Absorption curve of the products of reaction of HCl and $(C_6H_5)_2NN(C_6H_5)_2$ in EPA at low temperature; 2, absorption curve of $(C_6H_5)_2N^+$. In both cases the vertical scale is arbitrary.

The difficulties encountered in establishing the presence of $(C_6H_5)_2N^+$ seem to be attributable not merely to its remarkable instability but also to the small contribution that it makes to the total absorption. This is not due to a small absorption coefficient; presumably this ion and the chloride ion are in equilibrium with diphenylchloramine according to the equation

$$(C_6H_5)_2NCl \rightleftharpoons (C_6H_5)_2N^+ + Cl^- \qquad (3)$$

the diphenylchloramine being ionized only to a small extent. The situation is quite analogous to that of triphenylchloromethane in such a solvent as chlorobenzene.

Summary

Of the many reactions that are ordinarily observed when acid is added to tetraphenylhydrazine, none is the initial reaction. The first process, which occurs rapidly even near the temperature of liquid air, is the formation of $(C_6H_5)_2N^+$, which we have identified by its absorption spectrum. If tetraphenylhydrazine is assumed to be in rapid equilibrium with the positive and negative diphenylnitrogen ions, the effect of an acid is to remove the negative ion and thus cause accumulation of the colored positive ion, a considerable part of which, however, presumably combines with chloride ion to form colorless diphenylchloramine. The chloramine and its positive ion are too unstable to be observable except at extremely low temperatures.

A Study of Heterogeneous Equilibria in Aqueous Solutions of the Sulfates of Tetravalent Vanadium at 30°

By Charles S. Rohrer, Oscar E. Lanford and Samuel J. Kiehl

Introduction

The hydrates of the sulfates of tetravalent vanadium reported in the literature by previous investigators are divided into two series by Mellor[1]: the one, $VO_2 \cdot SO_3 \cdot xH_2O$ and the other $2VO_2 \cdot 3SO_3 \cdot xH_2O$. However, we believe that he entertains some doubt as to the number of hydrates in each, for he states: " . . . some of them may be mixtures representing arbitrary states in the process of dehydration." This uncertainty is more clearly substantiated if one considers the water ratio of each series. There are reported[2-5] for the first series the following molecular ratios of H_2O/VO_2·

(1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Company, New York, N. Y., 1929.

(2) J. J. Berzelius, Phil. Mag., 10, 321 (1831); 11, 7 (1832).

(3) B. W. Gerland, Chem. News, 34, 2 (1876); Ber., 9, 869 (1876); 10, 2109 (1877); 11, 104 (1878).

(4) J. W. Crow, J. Chem. Soc., 30, 453 (1876).

(5) I. Koppel and E. C. Behrendt, Z. anorg. Chem., 35, 154 (1903).

SO_3: 0, 1, 1.5, 2, 2.5, 3, 3.5, 5, 6.5, and for the second series, the molecular ratios of $H_2O/2VO_2$· $3SO_3$: 0, 1, 1.5, 2, 3, 4, 6, 14 and 16.

Doubtless in many of the preparations, since the products depended upon drying at various temperatures up to 360°, it is quite possible that intermediate states of incomplete hydration were reached. For, at 360° insoluble $VO_2 \cdot SO_3$ is invariably precipitated from concentrated sulfuric acid. Then, too, Gerland[3] dried the pentahydrate at 100° and reported not only $VO_2 \cdot SO_3 \cdot 2.5H_2O$, but also $VO_2 \cdot SO_3 \cdot 1.5H_2O$ by prolonged heating at that temperature.

By the same procedure Koppel and Behrendt[5] reported $VO_2 \cdot SO_3 \cdot 2.5H_2O$ and $VO_2 \cdot SO_3 \cdot 2H_2O$. If, however, the heating was done at 125°, they obtained $VO_2 \cdot SO_3 \cdot 1.5H_2O$ and $VO_2 \cdot SO_3 \cdot H_2O$ at 150°. Moreover, by heating $2VO_2 \cdot 3SO_3 \cdot 4H_2O$ in the second series at from 140 to 160° they obtained