An attempt has been made to measure the dissociation pressure of calcium nitride at temperatures somewhat above 1000°. Reproducible pressure readings were obtained of the order of magnitude of $0.3\text{–}5.5 \times 10^{-4}$ cm. The results are consistent with an energy change accompanying the reaction of 113,250 calories, which agrees well with the heat of formation of calcium nitride at ordinary temperatures, as determined by Guntz and Bassett. It is pointed out that in all probability calcium could not have been present as a third phase in this equilibrium.

In a system consisting initially of a mixture of calcium, calcium nitride and calcium hydride, an equilibrium was found to exist at temperatures in the neighborhood of 1000°. Only hydrogen was present in the vapor phase. After continued heating at 870°, the hydrogen was ultimately completely absorbed.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A PHOTOCHEMICAL STUDY OF ACETYL-CHLORO-AMINOBENZENE[1]

BY J. H. MATHEWS AND R. V. WILLIAMSON

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In connection with a series of investigations which were being carried out in this Laboratory, there was needed a light sensitive compound whose changes could be easily and accurately followed. The compound, acetyl-chloro-aminobenzene, appeared to be one that might serve the purposes for which these compounds were wanted.

Blanksma[2] appears to be the first to have noted that the compound was sensitive to light and he stated, "The reaction is much accelerated by light and it appears to be a general rule that the radicals Br, Cl, NO_2, NO and O attached to nitrogen, change places, under the influence of sunlight, with an H atom in the nucleus."

Chattaway and Orton also made some velocity measurements on the transformation of the compound in sunlight.[3] But there appears to have been no study made of the effect of light on the transformation of the compound under conditions such that the light intensity and conditions of the experiments were under control. Therefore, the present investigation was undertaken for the purpose of obtaining velocity measurements under conditions which could be duplicated.

[1] This paper constitutes the major part of a thesis submitted by R. V. Williamson in partial fulfilment of the requirements for the degree of Master of Science at the University of Wisconsin.

[2] Blanksma, *J. Chem. Soc.*, **82**, 646 (1902); *Rec. trav. chim.*, **21**, 290 (1902).

[3] Chattaway and Orton, *Proc. Chem. Soc.*, **18**, 200 (1902).

The compound has attracted considerable attention in connection with the theory of solutions. With dil. hydrochloric acid the compounds R.CO.NR′Cl undergo a molecular rearrangement in which the chlorine attached to the nitrogen exchanges places with one of the hydrogen atoms of the benzene ring. This reaction may be represented as follows: $CH_3CONClC_6H_5 + HCl = CH_3CONHC_6H_4Cl + HCl$.

From this equation, it is apparent that the hydrochloric acid acts as a catalyst, as the only change in the substances present has been a molecular rearrangement of the acetyl-chloro-aminobenzene to chloro-acetanilide. The above reaction is a monomolecular reaction in the presence of dil. hydrochloric acid but does not follow the monomolecular equation at higher concentrations of acid. It follows the equation for a bimolecular reaction in the presence of hydrobromic acid. These data have led Acree,[4] Senter[5] and others to propose the "Dual Theory" of reaction in solution, that is, both ions and molecules react when a reaction takes place in solution.

Harned and Seltz have opposed this "Dual Theory" and have shown that the velocity of rearrangement of acetyl-chloro-aminobenzene to *p*-chloro-acetanilide by hydrochloric acid is proportional to the product of the hydrogen and chlorine ions.[6]

In view of the theoretical importance of the catalytic reactions which this compound undergoes in the dark it may be of interest to present the data obtained in regard to its behavior under the influence of light from a quartz mercury-vapor lamp in different solvents and under various conditions.

Preparation and Purification of Chemicals Used

The acetyl-chloro-aminobenzene was prepared by Slosson's method.[7] The melting point of the compound was 89°. All chemicals used were prepared by purification of the standard brands of C. P. materials.

Apparatus

A quartz mercury-vapor lamp of a common commercial type was used as the source of illumination. On each side of the lamp was placed a quartz flask for holding the solution to be examined. All flasks were of the same size and each flask was provided with a mechanical stirrer which operated from the same pulley so as to produce the same agitation in each flask. A thin sheet of water flowed from the constant-temperature reservoir over the surfaces of the flasks to maintain them at the desired temperature. The electrical circuit was provided with a variable resistance for controlling the current passing through the lamp. The apparatus was set up in a dark room and all the work connected with the experiments was done in the dark room, with the help of electric lights.

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[4] Acree and Johnson, *Am. Chem. J.*, **37**, 410 (1907); **38**, 258 (1908).

[5] Senter, *J. Chem. Soc.*, **91**, 467 (1907).

[6] Harned and Seltz, THIS JOURNAL, **44**, 1475 (1922).

[7] Slosson, *Ber.*, **28**, 3265 (1895).

Procedure

By trial experiments the exact position of the flasks, with respect to the light, necessary to produce duplicate results when portions of the same solution were placed in each flask was determined. The flasks were then marked and the necessary measurements made to allow them to be removed from their clamps and replaced in exactly the same positions. They were filled with definite amounts of the solution to be examined, the stirrers started, the water for controlling the temperature was turned on, a light shield inserted between the light and the flask and then the current was turned on the lamp. When the lamp had reached its maximum intensity, a sample of 2 cc. was removed from the 100cc. flask for the initial titration, and then the light shield was removed. At definite time intervals other samples were removed for titration. A check was always carried on at the same time, to determine the velocity of the dark reaction, by means of a similar flask painted with asphaltum varnish to protect the solution from the light. The velocities of the reactions of two different solutions were compared by placing one solution in Flask 1 and the other in Flask 2.

The course of the reaction was followed by titrating with sodium thiosulfate solution the iodine liberated when the sample was allowed to run into an excess of potassium iodide acidified with hydrochloric acid. The acetyl-chloro-aminobenzene liberates iodine from a potassium iodide solution acidified with hydrochloric acid, whereas the transformation product, *p*-chloro-acetanilide does not.

The temperature of the water flowing over the flasks and the voltmeter and ammeter readings were recorded after each titration. The following is a typical example of the method of recording the data and shows the variation in temperature and voltage during an experiment.

Table I

Typical Data

Time	Volts	Amps.	Temp. °C.	$Na_2S_2O_3$ Cc.
9.25	67	3.0	21.0	8.70
9.40	66	3.05	21.4	7.55
9.55	65.5	3.1	20.9	6.45
10.10	68	3.05	20.6	5.40
10.25	68	3.1	20.6	4.28
10.40	69.5	3.1	20.7	3.20
10.55	65	3.1	20.9	2.35
11.05	69	3.1	20.7	1.90
11.15	69	3.1	20.6	1.40
11.30	70	3.1	20.7	1.20
11.40	68	3.1	20.9	1.10

This is a fair example of the variation in voltage and temperature but the amperage is an average reading of the ammeter. The amperage remained constant for the most part at the point indicated, but occasionally showed temporary fluctuations of ± 0.2 ampere.

Three experiments are recorded below showing the velocity of the dark reaction when the compound was dissolved in dil. acetic acid, and the degree of accuracy obtainable when portions of the same solution were placed in each flask.

Expt. 1.—1.6950 g. of acetyl-chloro-aminobenzene was dissolved in 100 cc. of glacial acetic acid and diluted to 1 liter with distilled water. The solution was kept in a brown bottle which was placed in the ice chest with cracked ice surrounding it. We shall call this "Solution A." Samples of Solution A were titrated from time to time to get the velocity of transformation in the dark.

Time in min.	0	21.60	42.90	55.38	69.24
$Na_2S_2O_3$, cc.	19.77	19.64	19.49	19.33	19.13

Expt. 2.—Expts. 2 and 2′ were made to show that the two flasks were so adjusted that the velocity of the reaction was the same when they contained portions of the same solution. The solution in this experiment was made by taking 90 cc. of Solution A and diluting it to 180 cc.

Temp. 3.01°. Volts 68.7. Amps. 3.0

Time in min.	0	44	96	137	206	292	340	617
$Na_2S_2O_3$, cc.	9.85	8.10	6.57	5.50	3.98	2.52	2.00	0.25
Monomol. vel. const. $\times 10^3$. . . .	..	1.9	1.8	1.9	1.9	2.0	2.0	1.9

Expt. 2′.—This experiment is a duplicate of Expt. 2 except that the solution was contained in the flask which was on the opposite side of the lamp.

Time in min.	0	45	97	163	217	300	341	617
$Na_2S_2O_3$, cc.	9.85	8.00	6.45	4.78	3.64	2.29	1.85	0.29
Monomol. vel. const. $\times 10^3$. . . .	..	2.0	1.9	1.9	2.0	2.1	2.2	2.0

These experiments show that the reaction follows the equation for monomolecular reactions in dil. acetic acid solution under the influence of light, which is characteristic of photochemical reactions. When the compound was dissolved in other solvents, however, it was not always possible to calculate the velocity constant.

Experimental Part

In Fig. 1, Curves I and II compare graphically the velocities of reaction for two solutions of 0.01 *M* acetyl-chloro-aminobenzene in 10% acetic acid solution plus 2% sodium acetate and in 10% acetic acid alone, respectively, when exposed to ultra-violet light. The curves show that practically no effect was produced by the addition of the sodium acetate. The velocity constants calculated by the equation for monomolecular reactions were 0.0064 and 0.0067; the difference is within the experimental error.

Curves III and IV, Fig. 1, are duplicate determinations for the same strength, and under the same conditions as Curves I and II, except that benzene was used as the solvent.

Curve V, Fig. 1, is a duplicate of Curves III and IV except that the benzene used as a solvent was recovered from the solutions used in producing Curves III and IV. The benzene was recovered by distilling it from the solute. Evidently some compound distilled with the benzene which catalyzed the reaction and speeded it up to a very marked degree. No effort was made to determine the exact reason for this behavior.

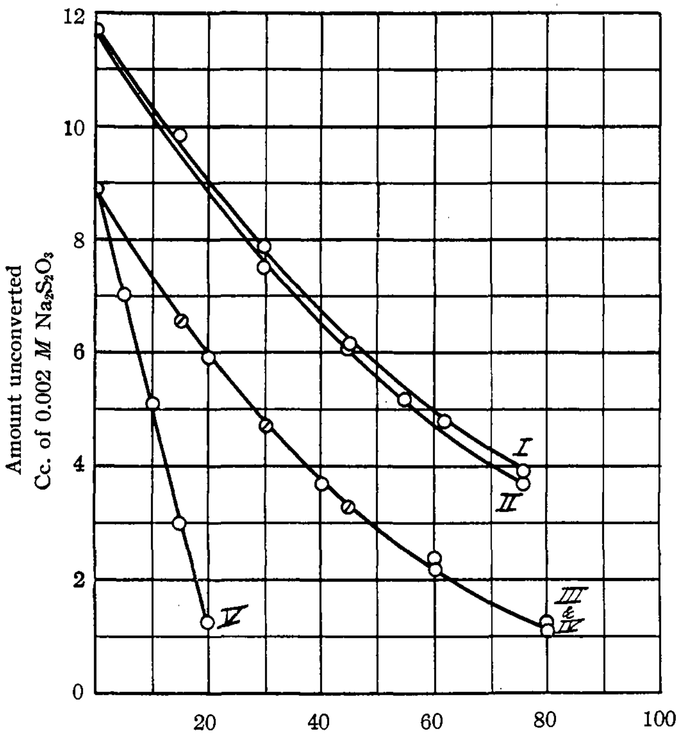

Fig. 1

Curves I and II, Fig 2, show the relative transformation of a 0.01 *M* and 0.02 *M* solution in 10% acetic acid under the influence of light of the same intensity. While the stronger solution showed a slightly greater amount transformed in unit time, the velocity constant was only 0.0009 as compared with 0.0017 in the more dilute solution. That is, the velocity constant for the solution of double strength had a value of one-half that for the more dilute solution.

Curve III, Fig. 2, shows the comparative amount transformed when the solvent is glacial acetic acid as compared to 10% acetic acid in Curves I and II. It shows also that the reaction continues with practically no change in velocity when the light is extinguished. This solution in glacial acetic acid showed no change during a period of one-half hour previous to turning on the light. However, when the light once initiated the reaction, it proceeded without diminution when the light was extinguished. This was found to be true in other solutions where water was absent.

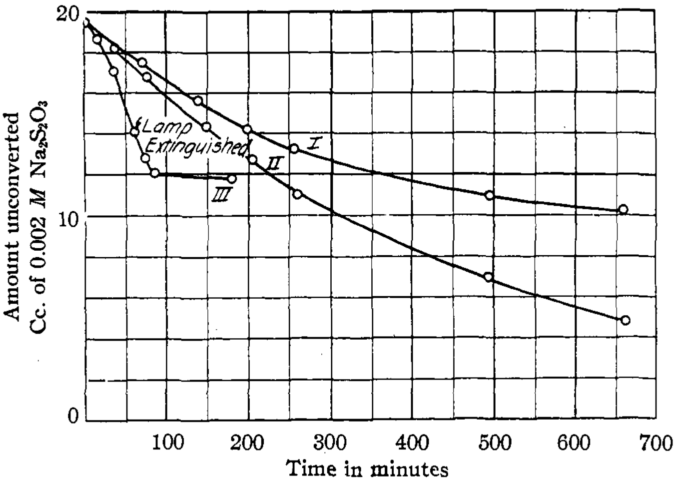

Fig. 2

In view of the fact that hydrochloric acid catalyzes the transformation in the dark it was thought that perhaps the reaction would be extremely sensitive in the light in the presence of this acid. Curve I, Fig. 3, shows the amount of transformation of a 0.01 *M* solution in 10% acetic acid containing 45% *N* hydrochloric acid in the dark as compared with the light reaction in 10% acetic acid in Curve II, the light reaction in 10% acetic acid plus 25% of *N* hydrochloric acid in Curve III and to the light reaction of 10% acetic acid containing 45% of *N* acid in Curve IV. The broken line curve represents the sum of the dark reaction in the presence of 45% of *N* hydrochloric acid plus the light reaction in 10% acetic acid. This indicates that the light reaction in the presence of hydrochloric acid is greater than the sum of the light reaction in dil. acetic acid plus the dark reaction produced by hydrochloric acid.

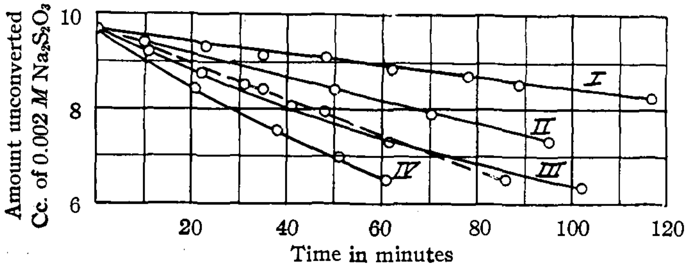

Fig. 3

Curve I, Fig. 4, shows the transformation in 10% acetic acid under the action of light compared with the dark reaction in 10% acetic acid plus 2% of 0.25 N hydrobromic acid as shown in Curve II, and the light reaction in 10% acetic acid plus 2% of 0.025 N hydrobromic acid, Curve III. The broken line represents the sum of the individual reactions represented by Curves I and II. From these results the light reaction in 10% acetic acid solution containing 2% of 0.25 N hydrobromic acid is shown to be practically equal to the sum of the light reaction in 10% acetic acid plus the dark reaction produced by the presence of the hydrobromic acid in the 10% acetic acid solution.

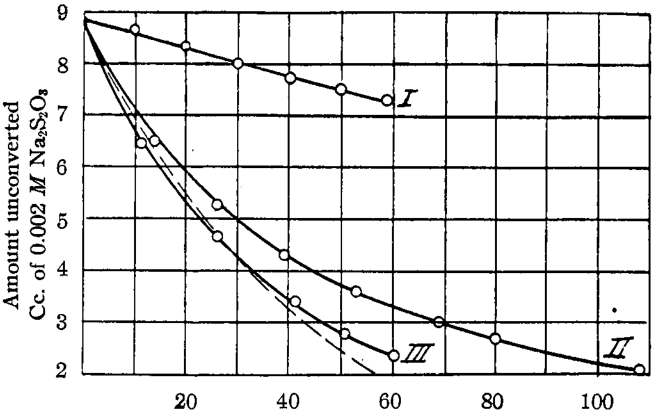

Fig. 4

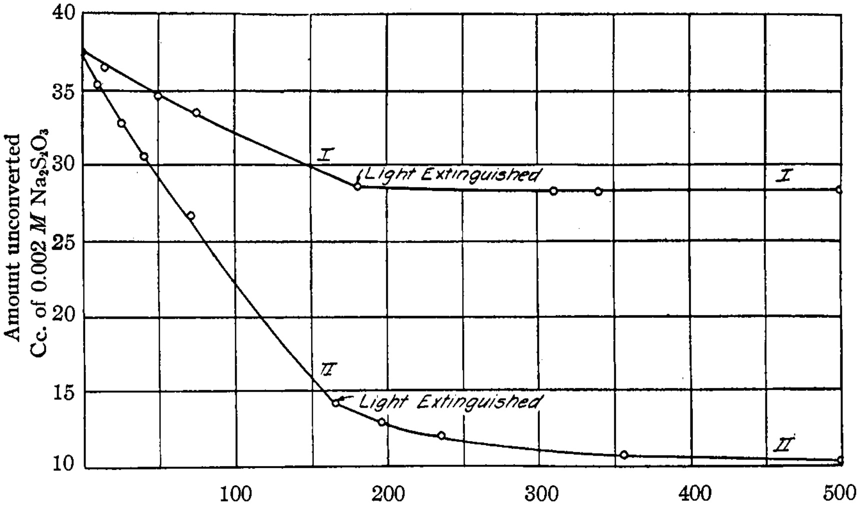

Fig. 5

Curve I, Fig. 5, shows the result of illuminating with ultra-violet light a 0.04 *M* solution of acetyl-chloro-aminobenzene in 10% acetic acid in comparison with a solution of the same strength in benzene as shown in Curve II. It is apparent that the acetic acid solution ceased to react as soon as the light was turned off but the reaction in the benzene solution proceeded slowly for some time after the light was extinguished. Concordant velocity constants were calculated for both the acetic acid and the benzene solutions. The velocity constant as calculated by the monomolecular equation was 0.0023 for the benzene solution and 0.00065 for the acetic acid solution.

Some experiments were carried out to determine the effect of concentration of the solute in benzene as solvent and results similar to those found in acetic acid were obtained, as shown in Curves I and II, Fig. 2.

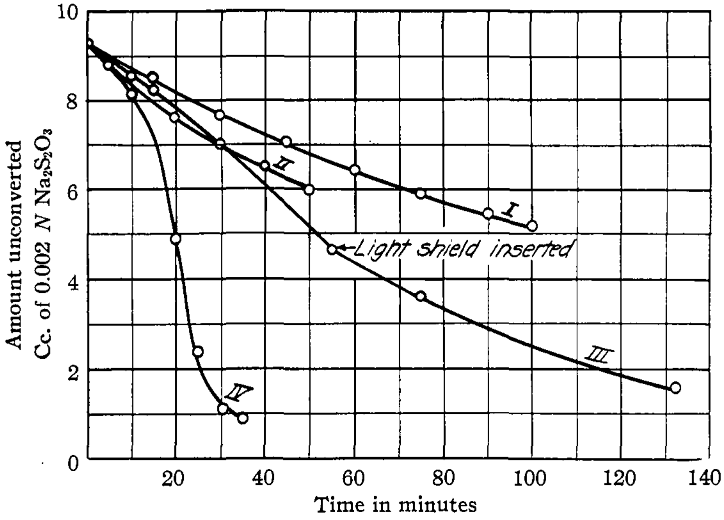

Fig. 6

Curves I and II, Fig. 6, show the effect of temperature on the velocity of transformation of a 0.01 *M* solution in 95% alcohol. The temperature of the solution in Curve I was 0.7° and that in Curve II was 21.1°.

Curves III and IV show the effect of temperature on an absolute alcohol solution of 0.01 *M* concentration. The temperature of the solution for Curve III was 0.3° and for Curve IV was 21.2°. It will be noticed that the effect of temperature on the 95% alcohol solution is very much less marked than on the absolute alcohol solution. This is in accord with the usual low temperature coefficients of photochemical reactions. Dilute solutions of acetyl-chloro-aminobenzene in alcohol containing small amounts of water act like true photochemical reactions, as is shown in Fig. 7, Curve III, whereas in absolute alcohol solutions the reactions are not true photochemical reactions, since the reaction proceeds without the light after the reaction is initiated, as is shown by Curves II and IV, Fig. 7. Therefore, the temperature coefficient of the reaction in absolute alcohol is equal to the coefficient for an ordinary chemical reaction.

In Fig. 7, the presence of small amounts of water is shown to have the effect of a negative catalyst. Curve II shows the velocity of transformation of a 0.04 *M* solution in absolute alcohol with and without the light. No diminution whatever is noted when the light is extinguished after the reaction is initiated, but the addition of a small amount of water toward the end of the reaction causes a marked decrease in the velocity of transformation. Curves III and IV show the effect of extinguishing the light when the solvent is 95% and partially dehydrated alcohol, respectively, and the concentration of the solute is only 0.01 *M*. Curves I and II show the results obtained with a stronger solution (0.04 *M*) in 95% and with partially dehydrated alcohol, respectively. The alcohol used in the solution for Curves II and IV was treated with anhydrous copper sulfate until only traces of water remained in the alcohol, but of course was not completely anhydrous. From these curves, it is seen that water retards the velocity of transformation, but its effect is reduced as the strength of the acetyl-chloro-aminobenzene is increased. For

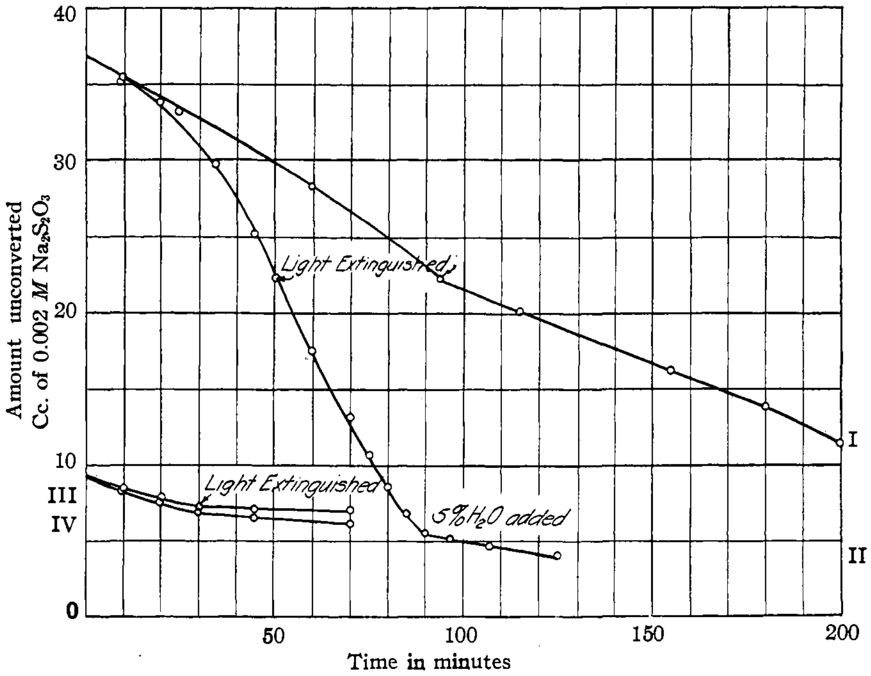

Fig. 7.

example, the reaction stops completely in a 0.01 *M* solution in 95% alcohol when the light is removed, as shown by Curve III, but is only slightly retarded when the concentration is increased to 0.04 *M*, as shown by Curve I.

Discussion of Results

Acetic Acid Solutions.—Others have shown that the transformation of acetyl-chloro-aminobenzene in dil. acetic acid solution is very slow in the absence of light. When hydrochloric or hydrobromic acid is added to the solution, however, the decomposition proceeds in the dark. With hydrochloric acid, the reaction is monomolecular, at least within certain limits of concentration, whereas with hydrobromic acid it is bimolecular.[4] Our experiments show that a 0.01 *M* solution in 10% acetic acid containing 1% of 0.25 *N* hydrochloric acid showed no appreciable decomposition at the end of 3 hours. On the other hand, a solution containing 1% of hydrobromic acid in a 10% acetic acid solution of the same strength of acetyl-chloro-aminobenzene showed a marked decomposition. A higher concentration of hydrochloric acid, for example a solution containing 25% of *N* hydrochloric acid, produced rapid transformation in the dark. It appears from these experiments, therefore, that a certain concentration of hydrochloric acid is necessary before the transformation takes place.

The light reaction in 10 or 20% acetic acid appears to follow the equation for a monomolecular reaction, which is characteristic of photochemical reactions, but the velocity constant is not independent of the initial concentration of the solute, as is the case with monomolecular reactions. The velocity of the light reaction is the same whether the solution contains 10 or 20% acetic acid.

The sum of the velocities of the dark reaction with hydrobromic acid as catalyst plus the light reaction in 10% acetic acid is the same as for the light reaction in the case of a 10% acetic acid solution containing the same concentration of hydrobromic acid. The light reaction in the case of a 10% acetic acid solution containing hydrochloric acid as catalyst was somewhat greater than the sum of the light reaction in 10% acetic acid and the dark reaction with hydrochloric acid as catalyst.

In dilute acetic acid (10 or 20%) the transformation proceeds only under the influence of light but in a glacial acetic acid solution the reaction proceeds without the action of light after the reaction is started by the light.

Alcoholic Solutions.—Alcoholic solutions of acetyl-chloro-aminobenzene were found to behave similarly to those in acetic acid. 0.01 *M* solutions in alcoholic solvent containing as much as 95% of alcohol appeared to give true photochemical reactions in that they proceeded only under the influence of light, showed a temperature coefficient of 1.23 and conformed to the equation for monomolecular reactions. The velocity constant was not independent of the concentration, however, but was only about half as great when the concentration of solute was doubled, as was also the case in dil. acetic acid.

When the concentration of solute in 95% alcohol was increased to 0.04 *M*, however, the reaction ceased to be truly photochemical but continued after the light was extinguished, although at a diminished velocity.

In absolute alcohol the compound was stable in the dark but after the transformation was initiated by the light the reaction proceeded with undiminished velocity when the light was extinguished. The velocity was very much greater in the absence of water in both alcoholic and acetic acid solutions.

The temperature coefficient for the reaction in absolute alcohol was about 1.6 as compared with 1.23 for the reaction in dil. alcohol, which is characteristic of the difference between photochemical reactions and ordinary chemical reactions.

Benzene Solutions.—These experiments show that the velocity of transformation of acetyl-chloro-aminobenzene, when dissolved in benzene, under the influence of the light from a quartz mercury-vapor lamp, as well as the decomposition under the action of the light, is between that for dil. acetic acid and absolute alcohol solution. The velocity of the light reaction in benzene solution is about the same as in 95% alcohol. The velocity constants can be calculated for all concentrations tried by means of the equation for monomolecular reactions. The velocity constant is not independent of the concentration of the solute, however.

When the transformation is started in benzene solution by the action of light and the lamp is then extinguished, the reaction does not stop immediately as it does in 10% acetic acid solution of the same concentration nor does it continue without diminution as it does in an absolute alcohol solution, but the velocity decreases very rapidly for a short time and then very slowly.

Summary

The decomposition of acetyl-chloro-aminobenzene under the influence of the light from a quartz mercury-vapor lamp has been studied in various solvents. The solvent has been found to have a marked effect on the behavior of the reaction.

When water is added to an alcoholic or glacial acetic acid solution of acetyl-chloro-aminobenzene the velocity of the light reaction is greatly diminished. It also causes the reaction to proceed as a true photochemical reaction, whereas in the absence of water the reactions in absolute alcohol and glacial acetic acid solutions proceed without the action of light after the reaction is once initiated.

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