ring and if the extinction coefficient can be assumed to be equal to that of *trans*-1,2-dimethylcyclohexane, namely, 25 l. cm.$^{-1}$ mole^{-1} as calculated[46] from infrared spectra, then G (ring-link) can be estimated from the slope of the curve of optical density *versus* radiation dose for Marlex-50 to be 1.5. This is a surprisingly high value as it is the same order of magnitude as G(Vl), but it may be without quantitative significance because of the uncertainty concerning the nature of the absorbing group. For example, the absorbing group might possibly be a disubstituted cyclopropane.

It is difficult to measure the temperature coefficient of the optical density at 10.1 μ inasmuch as the much larger and overlapping absorbance due to the vinyl group does not disappear with irradiation at liquid nitrogen temperature. Some of this absorbance does disappear on warming to room temperature; hence a rough estimate can be made of the growth of the optical density at 10.1 μ. Two estimates for liquid nitrogen temperature irradiations of Marlex-50 (infrared spectra studied at room temperature) agreed fairly well with each other and demonstrate a temperature effect about equal to that for cross-linking (cross-linking will be discussed in a later paper). Thus, from this standpoint ring-link formation is more akin to cross-linking than to vinylene formation.

The slope of the curve for Marlex-50 is 1.35 times as great as that for the Ziegler polyethylene Q-911. As the increase in absorbance at 10.1 μ cannot be measured in the case of B-3125, if indeed, it exists at all, one thus sees a good correlation between the crystallinity of the polyethylene and rate of formation of ring-links. This trend is opposite to that of cross-linking inasmuch as Miller and Lawton[47] have noted a lower cross-linking efficiency (as determined from solubility measurements) for highly crystalline Marlex-50 than for a low density polyethylene.

D. Comparison with Results of Others.—In this paper we shall not attempt a material balance calculation; instead a comparison with results of others will be given. Miller and Lawton[47] adopt Miller, Lawton and Balwit's[12] value of G(*trans*-CH=CH–) equal to 2.2 and state that it is independent of temperature and crystallinity. They assume that the rate of *trans*-vinylene production is linear up to 50 megaroentgen/g. (29.0×10^{20} e.v./g.). From the data of Fig. 5 and Table IV it is clear that the linear rate of vinylene production occurs only to about 8 megaroentgen/g. and that the efficiency of vinylene formation increases with the crystallinity. Charlesby and Davison[9] found 1.3 for G(*trans*-CH=CH–), an integral value for 20 megaroentgen.

The values of G(*trans*-Vl) given in Table IV are intermediate between the values of Charlesby and Davison, and Miller, *et al.* However, it should be noted that Miller and Lawton[47] take 5.7 for $G(\text{H}_2)$ while Charlesby and Davison[9] found 3.1 and we, 4.0 (details to be published later). Miller and Lawton neglect the destruction of the initial unsaturation in computing a material balance. Charlesby and Davison give 0.74 for G(-vinylidene) while our result from Table II is 3.7 for the initial value. Charlesby and Davison's result represents an average value over 20 megaroentgen.

Acknowledgments.—This research was supported by the U. S. Atomic Energy Commission. We are grateful for gifts of materials from the Phillips Petroleum Company, The Dow Chemical Company and E. I. du Pont de Nemours and Company. R. H. Hammaker made the density measurements.

EVANSTON, ILLINOIS

---

[46] "Catalog of Infrared Spectral Data" of the Amer. Petroleum Institute Research Project, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

[47] A. A. Miller and E. J. Lawton, Preprints of Papers, Division of Paint, Plastics and Printing Ink Chemistry, A. C. S., Vol. XVII, No. 2, Sept. 1957.

[CONTRIBUTION FROM THE BIOPHYSICS LABORATORY, TULANE UNIVERSITY]

A Magnetic Study on the Photodecomposition of *p*-(N,N-dimethylamino)-benzenediazonium Chloride

BY E. A. BOUDREAUX AND E. BOULET

RECEIVED SEPTEMBER 26, 1957

A study of the mechanism of photodecomposition for the inorganic stabilized diazonium salt, *p*-(N,N-dimethylamino)-benzenediazonium chloride–zinc chloride dihydrate, in both buffered and non-buffered aqueous solutions has been investigated by magnetic susceptibility measurements. These measurements were conducted on the samples during the time of irradiation with ultraviolet light. The results indicate the presence of free radicals as intermediates in the formation of the products. The molar concentrations of free radicals calculated from the data are approximately 7.3×10^{-4}, 1.1×10^{-3} and 1.8×10^{-3} mole per liter, respectively, for two buffered solutions having *p*H 1.7 and 3.5 and for a non-buffered solution with *p*H 3.5.

The mechanism of the decomposition of diazonium salts has remained in a controversial state for some time.[1] Waters and his followers[2] present very strong evidence for a free radical mechanism, but Hodgson and his co-workers[3-6] give evidence for an ionic mechanism. However, the views of

---

[1] K. H. Saunders, "The Aromatic Diazo Compounds," Edward Arnold and Co., London, 1949, p. 105.

[2] W. A. Waters, *J. Chem. Soc.*, 113, 2007, 2014 (1937); 1077 (1938); 864, 1805 (1939).

[3] H. H. Hodgson, S. Birtwell and J. Walker, *ibid.*, 770 (1941).

[4] H. H. Hodgson, *ibid.*, 348 (1948).

[5] H. H. Hodgson, *Chem. and Ind.*, 774 (1947).

[6] H. H. Hodgson, *J. Soc. Dyers Colourists*, **64**, 99 (1947).

Hodgson were strongly refuted by Hey and Waters.[7]

Perhaps the most recent and reliable evidence available that would offer some solution to this dilemma is that of Horner and Stohr.[8] These two investigators have performed some very thorough work from which they conclude that the mechanism of decomposition of diazonium salts involves both free radical and ionic mechanisms, depending upon the environment and materials reacted.

In an effort to present further evidence which would aid in solving this problem, it was decided that a magnetochemical investigation should be conducted on the photodecomposition of a diazonium salt. Such a study would yield information as to the presence of free radicals during the decomposition, provided the reaction rate is not too fast.

The material selected for this investigation was the stabilized diazonium salt, *p*-(N, N′-dimethylamino)-benzenediazonium chloride–zinc chloride dihydrate. This compound was chosen mainly because of its ready availability from the manufacturer, Ringwood Chemicals, Inc., Ringwood, Illinois.

Experimental

Materials.—The diazonium salt used was as is indicated above. The buffers employed in the investigation were McIlvaine's standard buffer solutions of citric acid and disodium hydrogen phosphate, for which procedures of preparation and *p*H tables are given in most chemical handbooks.

The light source for the irradiation of the solutions was supplied by a 100 watt model AH-4 General Electric mercury vapor lamp. All *p*H measurements were conducted with *p*H paper having increments of 0.2 to 0.5 unit.

The *p*-benzoquinone which was employed as a free radical scavenger was obtained from Eastman Organic Chemicals, Inc., Rochester, New York.

The light source, timer and air blower, which was incorporated to keep the lamp cool, were all connected to a 115 volt, 60 cycle, constant voltage transformer to ensure constant electrical operation.

Magnetic Measurements.—The magnetic susceptibility measurements were made with a Gouy balance according to standard procedures. The apparatus which was constructed in our laboratory consists of a Christian Becker analytical balance equipped with an optical system for direct reading of the scale. The balance was converted so that a sensitivity of 0.02 mg. could be maintained. A permanent magnetron magnet having a constant field of 4985 gauss also was employed.

The balance was calibrated in the usual manner with equilibrium water and pure benzene, for which standard susceptibilities are known. Accuracy in determining ΔW, the difference between the weight in the magnetic field and the weight with no field, was reproducible to 0.05 mg. where the units of ΔW are in 10^{-4} g.

Measurements were conducted with the ultraviolet lamp mounted perpendicular to both the sample and the magnetic field, so that the beam of light could be focused directly on the entire sample. Values of ΔW were then recorded at various intervals of irradiation time.

All solutions investigated were of a *p*-(N,N-dimethylamino)-benzenediazonium chloride–zinc chloride dihydrate concentration of 10% by weight.

Results and Discussion

Each of curves A, B and C represents the average of two determinations for each of the solutions investigated. The results were reproducible within experimental error. Curve A includes data which were obtained for a buffered solution of *p*H 1.7. This curve shows a 5.2% decrease in diamagnetism.

Similar data for curve B, in which a buffered solution of *p*H 3.5 was employed, shows a decrease in diamagnetism of only 3.2%. The results in curve C were obtained with a non-buffered solution of *p*H 3.5. This solution gave a maximum decrease in diamagnetism of 10.4%.

These results could be attributed to the presence of free radicals during the photodecomposition of the diazonium salt. It is improbable that these results are due to paramagnetic impurities such as dissolved oxygen or air, or inorganic paramagnetic materials, for care was exercised in preparing the samples so that no dissolved air or foreign matter would contaminate them. The sample tubes were then sealed. In addition, Pascal's constants for the atoms in the chemical formula of the inorganic stabilized diazonium salt gave a molar susceptibility (-195×10^{-6}) near the experimental value (-200×10^{-6}) taken on the powdered solid.

On a solution buffered to *p*H 3.5 the exposure to light was interrupted in the time interval four to six minutes. ΔW determined in this interval was the same as that at zero time. Other solutions buffered to *p*H 3.5 whose exposures were interrupted in the intervals 11–14, 15–16 and 48–50 minutes, respectively, also gave ΔW values for these intervals which were the same as that at zero time. This indicates that the chemical species responsible for the observed data are of a transitory nature.

Finally, a series of determinations of ΔW were made on the non-buffered solution to which *p*-benzoquinone, a free radical scavenger, was added in 0.01 molar concentration. The results revealed no change in diamagnetism for a period of one hour of irradiation. Thus it is likely that free radicals are responsible for the results given in Fig. 1.

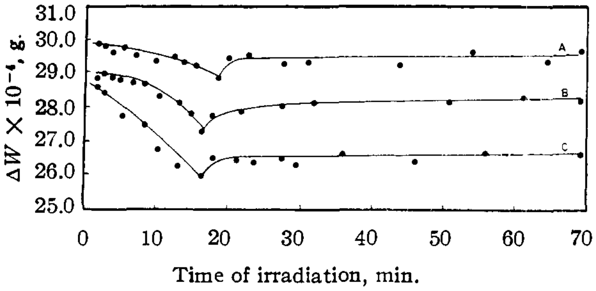

Fig. 1.—A plot of ΔW *vs.* time for various aqueous solutions of *p*-(N,N-dimethylamino)-benzenediazonium chloride–zinc chloride dihydrate, while being irradiated with the full spectrum of a General Electric 100 watt, AH-4 mercury vapor lamp. ΔW is the difference between weight of solution when in the magnetic field (4985 gauss) and the weight when in no field. All solutions were of concentration of 10% by weight of the above named compound. Curve A is for a buffered solution of *p*H 1.7. Curve B is for a buffered solution of *p*H 3.5. Curve C is for a non-buffered solution of *p*H 3.5.

It also should be noted from curves A and B that the rate at which the minimum is established is slower at the lower *p*H. This is also in accord with the results of Blumberger[9] and Haggerty and

---

[7] D. H. Hey and W. A. Waters, *J. Chem. Soc.*, 882 (1948).

[8] L. Horner and H. Stohr, *Chem. Ber.*, **85**, 993 (1952).

[9] J. S. P. Blumberger, *Rec. trav. chim.*, **49**, 276 (1930).

Hadler,[10] who found that the rate of decomposition of many diazonium salts increases with decreasing acidity.

During the course of the decomposition it was noticed that the first sign of nitrogen bubbles appears in the solution always between one and three minutes. This time interval corresponds to the initial change in slope in each of the three curves in Fig. 1. It was further noticed that a copious evolution of bubbles always appeared between 11 and 14 minutes, which corresponds to the minimum in each of the curves.

However, since ΔW is proportional to the density of the solution, a decrease in ΔW as observed with the appearance of bubbles in the solution, as well as the maximum decrease in ΔW observed at the time corresponding to the copious evolution of bubbles, also may be attributed in part to a decrease in the density of the solution caused by the production of nitrogen bubbles in the decomposition process. But the results obtained with the *p*-benzoquinone added to the solution seem to indicate that the minima observed in curves A, B and C of Fig. 1 are due to free radical formation, for the same "copious evolution of bubbles" that was observed between 11 and 14 minutes in the other solutions also was observed in this solution. However, the curve obtained from the plot of ΔW *vs.* irradiation time was completely horizontal and exhibited no minimum or breaks whatsoever. It would seem that if the decrease in the density of the solution with the formation of bubbles was alone responsible for the minima observed in curves A, B and C of Fig. 1, then a similar result also should have been observed in the solution to which the *p*-benzoquinone had been added. It is not to be denied, however, that a decrease in the density of the solution attending the formation of bubbles does contribute to the reduction in the observed ΔW, but *in lieu* of the results obtained it would seem that the extent to which this effect contributes in reducing the susceptibility of the solution will be relatively small compared to the decrease in diamagnetism produced by the paramagnetic free radicals. In truth, it is probably both of these effects which are responsible for the minima produced in the curves of Fig. 1.

From these observations it seems evident that free radical formation occurs with the evolution of nitrogen. Thus the free radical mechanism of Blumberger[11] is supported. Blumberger's mechanism

$$\begin{aligned} ArN_2Cl &\xrightarrow{h\nu} Ar\cdot + N_2 + Cl\cdot \\ &\longrightarrow ArCl + N_2 \end{aligned}$$

anism is given here, indicating only the main products of decomposition. The reaction which produces ArOH probably also occurs and zinc chloride and water also are present. In addition, since the whole spectrum of the lamp was used we recognize the possibility of multi reactions at various rates.

In order that a rough estimate of the concentrations of free radicals in the solutions might be obtained, we proceed as follows. Assuming that the observed decreases in ΔW for each of the curves in Fig. 1 are due solely to free radical formation, thus neglecting that part of the decrease that is produced by the change in density, for reasons given above, an estimate of the concentration of free radicals present in each of the solutions can be obtained in the following manner. It was found experimentally that a change in weight of 0.08 mg. corresponded to a mass susceptibility of 0.014×10^{-6}, thus a decrease in diamagnetism of 5.2% for curve B gives a ΔW of 0.15 mg. and the susceptibility corresponding to this ΔW will be given by a direct proportionality of ΔW to susceptibility provided the density remains substantially constant, which condition seems reasonably satisfied here as discussed above. Thus the mass susceptibility corresponding to a ΔW of 0.15 mg. is 0.026×10^{-6}. The most likely free radicals formed are $(CH_3)_2NC_6H_5\cdot$ and $Cl\cdot$, which have molecular weights of 121.2 and 35.5, respectively. Assuming that the amount of chlorine radical formed is the same as that of aryl radical, which, however, may seem unlikely in the steady state, but which assumption must be held if any quantitative estimate of free radical concentration is to be achieved, then the observed molar susceptibility for the free radicals can be obtained by the following procedure. Let X_{Ar} = the gram susceptibility of the aryl radical, then $(121.2)X_{Ar} = 35.5(0.026 \times 10^{-6} - X_{Ar})$. $\therefore (121.2)X_{Ar} + (35.5)X_{Ar} = 0.92 \times 10^{-6}$. $\therefore X_{Ar} = 0.0059 \times 10^{-6}$. The susceptibility of chlorine radical is given by $0.026 \times 10^{-6} - 0.0059 \times 10^{-6} = 0.0201 \times 10^{-6}$. Thus, $X_M = (121.2)(0.0059 \times 10^{-6}) + (35.5)(0.0201 \times 10^{-6})$. $\therefore X_M = 1.429 \times 10^{-6}$.

Since the susceptibility of a free radical with one unpaired electron is 1270×10^{-6} per mole, then the number of moles of free radicals produced corresponding to a 5.2% decrease in diamagnetism will be given approximately by

$$\frac{1.429 \times 10^{-6}}{1270 \times 10^{-6}} = 1.1 \times 10^{-3} + \text{ moles}$$

The same procedure also was applied to the results in curves A and C, giving molar concentrations of free radicals of 7.3×10^{-4} and 1.8×10^{-3} moles, respectively.

Although the results of this investigation seem to infer a free radical mechanism in the photodecomposition of *p*-(N,N-dimethylamino)-benzenediazonium chloride, it would nevertheless be worthwhile to extend the investigation to include paramagnetic resonance studies, since this would be a very sensitive means for detecting the free radicals even in relatively small concentrations.

New Orleans, Louisiana

---

[10] C. J. Haggerty and B. C. Hadler, This Journal, **54**, 1707 (1932).

[11] J. S. P. Blumberger, *Rec. trav. chim.*, **49**, 259 (1930).