

[CONTRIBUTION FROM THE IBM SAN JOSE RESEARCH LABORATORY, SAN JOSE, CALIF.]

Photolytic Decomposition of Aryldiazonium Salts. The *p*-Dimethylaminophenoxy Radical

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The photolytic decomposition of *p*-dimethylaminobenzenediazonium chloride in aqueous solution with pH above 5 leads to the formation of a paramagnetic species. The electron spin resonance spectrum is the same as that obtained on air oxidation of *p*-dimethylaminophenol in the same pH range. On the basis of this evidence as well as the e.s.r. spectrum, the structure of the radical could be established as being the *p*-dimethylaminophenoxy radical (III). This radical was also generated chemically by the oxidation of the phenol by the diazonium compound. Similarly, the *p*-diethylaminobenzenediazonium chloride was photolytically decomposed to yield the corresponding phenoxy radical. The nitrogen and ring proton hyperfine coupling constants are the same in both radicals. In the diethyl radical the alkyl spin density is much lower than in the dimethyl radical. Therefore, the inductive effects of the alkyl groups on the spin distribution are very small and the alkyl spin density is determined by hyperconjugation. In the diethylamino radical the rotation of the ethyl groups around the C-N bonds is restricted as compared to the case of the methyl groups of the dimethylamino radical. The e.s.r. spectra of these radicals are strongly dependent on the solvent used. In dimethyl sulfoxide-water solutions similar solvent polarization occurs, as observed by Fraenkel, *et al.*<sup>1</sup>

## Introduction

The role of radical mechanisms in the thermal and photolytic decomposition of aryldiazonium salts in aqueous and organic media is not completely understood. The occurrence of aryl radicals in the Gomberg-Bachmann and Meerwein reactions<sup>2</sup> and in the hypophosphorous acid reduction of aryldiazonium salts has been reasonably established.<sup>3</sup> In addition, DeTar<sup>4</sup> has shown the apparent presence of a radical chain mechanism in the thermal decomposition of benzenediazonium chloride in methanol-acetate-acetic acid buffer. A radical mechanism has been postulated to explain the formation of nitrobenzene and other products in the photolysis of *p*-nitrobenzenediazonium stannic chloride salt in methanol.<sup>5</sup> The work of Horner and Stohr,<sup>6</sup> however, indicates that both the thermal and photolytic reductive decomposition of aryldiazonium salts occur in various unbuffered alcohols. Such products can also be rationalized within the framework of a hydride transfer mechanism.<sup>7</sup> The possible presence of radicals in photolyzed solutions of diazonium salts is indicated by the magnetic susceptibility measurements of Boudreaux.<sup>8</sup>

The observations mentioned above led us to investigate the possible presence of paramagnetic species in the photolytic, thermal, or electrolytic decomposition of aryldiazonium salts. By using electron spin resonance, these radicals or radical ions should be detectable in those cases where their lifetimes are sufficiently long. We studied the photodecomposition of *p*-dimethylaminobenzenediazonium chloride because of the previous evidence<sup>8</sup> for paramagnetic species. As a comparison, the diethylamino compound was also investigated.

## Experimental

(1) **Materials. Diazonium Solutions.**—Aqueous solutions of the aryldiazonium salts were prepared from the corresponding zinc chloride double salts (Aldrich Chemical) by adding dilute

(1) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

(2) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., pp. 518-522.

(3) N. Kornblum, G. D. Cooper, and J. E. Taylor, *J. Am. Chem. Soc.*, **72**, 3013 (1950).

(4) (a) D. F. DeTar and M. N. Turetzky, *ibid.*, **77**, 1745 (1955); (b) **78**, 3925 (1956).

(5) W. E. Lee, J. G. Calvert, and E. W. Malmberg, *ibid.*, **83**, 1928 (1961).

(6) I. Horner and H. Stohr, *Chem. Ber.*, **85**, 993 (1952).

(7) N. C. Deno, H. J. Peterson, and G. S. Saines, *Chem. Rev.*, **60**, 7 (1960).

(8) E. A. Boudreaux and E. Boulet, *J. Am. Chem. Soc.*, **80**, 1588 (1958).

aqueous potassium hydroxide to remove the zinc and bringing the filtered solution to the appropriate pH by the addition of Beckman buffer solution or Coleman buffer tablets. Concentrations of the diazonium salts were in the order of 0.01 to 0.001 *M*.

***p*-Dimethylaminophenol.**—The methiodide of *p*-dimethylaminophenol was conveniently prepared by refluxing a mixture of 10 g. of *p*-aminophenol, 25 ml. of methanol, 180 g. of methyl iodide, and 10 g. of potassium carbonate for 18 hr. Concentrating and cooling the reaction mixture yielded 17 g. of crude product. This material was dissolved in methanol, treated with charcoal, filtered, and cooled to yield colorless crystals, m.p. 204-206°. This material was smoothly decomposed in the melt at 1 mm. pressure to yield a colorless crystalline sublimate, m.p. 73-75°; reported by Pechmann:<sup>9</sup> 74-76°. A vapor phase chromatogram of this material indicated no other material present as an impurity.

Dimethyl sulfoxide (Eastman), 2,6-di-*t*-butyl-4-methylphenol (Shell), the hydrochloride salt of *p*-*N,N,N',N'*-tetramethylphenylenediamine, and *p*-*N*-methylaminophenol hydrogen sulfate were used without further purification. *p*-Aminophenol was recrystallized from methanol.

(2) **Electron Spin Resonance Spectra.**—Solutions of diazonium salt, the phenol, and other materials were measured in a 1-mm. plane parallel quartz cell positioned in the resonance cavity of a Varian 100-kc. electron spin resonance spectrometer. In those cases in which the effect of air was determined, the solutions were deoxygenated by bubbling nitrogen through the solution before introduction into the cavity. Oxygen was introduced merely by exposing the solution to air or by bubbling oxygen through the solution before introducing the sample into the cavity. For the purpose of irradiation of the sample, the sample inside the cavity was exposed to the unfiltered light from a 100-watt high pressure mercury arc (Pek Labs). In some cases, better results were obtained by letting the solution flow slowly through the cavity cell.

In all cases, the second derivative of the resonance absorption was measured so as to eliminate slow drift due to the evolution of nitrogen in the diazonium decomposition and to obtain high sensitivity.

## Results and Discussion

**Photolysis of Diazonium Salt Solutions.**—The photolysis of aqueous basic solutions of *p*-dimethylaminobenzenediazonium cation (Ia) at pH values greater than 5 gave a strong electron spin resonance spectrum (Fig. 1). This same spectrum was obtained by the air oxidation of aqueous basic solutions of *p*-dimethylaminophenol (II) at pH greater than 5. These observations, together with an analysis of the electron spin resonance spectrum (*vide infra*), show unambiguously that the paramagnetic species is the *p*-dimethylaminophenoxy radical (III). Similarly, irradiation of basic aqueous solutions of *p*-dimethylaminobenzenediazonium cation

(9) H. Pechmann, *Chem. Ber.*, **32**, 3682 (1899).

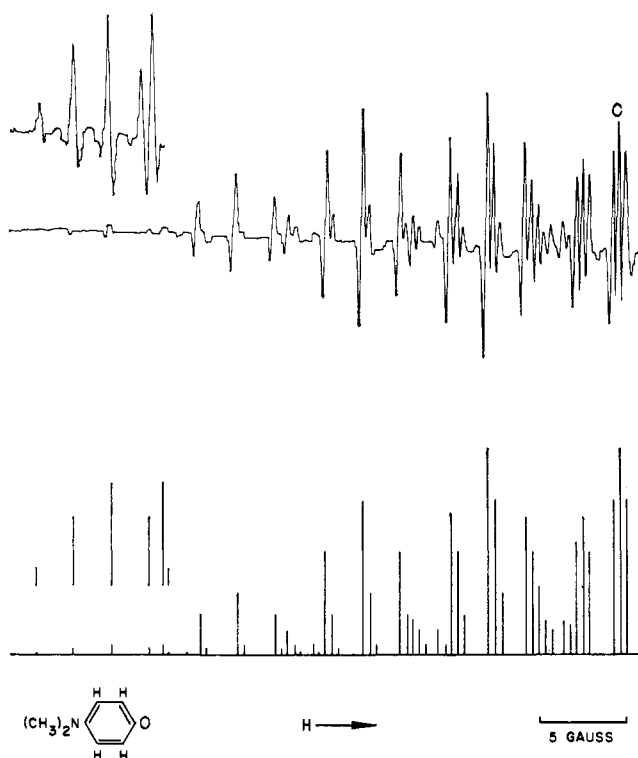
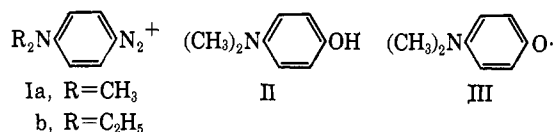


Fig. 1.—Second derivative of the electron spin resonance absorption spectrum of irradiated solutions of *p*-dimethylaminobenzenediazonium chloride. Reconstruction for  $a_N = 7.45$ ,  $a_{CH} = 2.14$ , and  $a_{CH_3} = 7.08$  gauss; C = center.

(Ib) gave the corresponding phenoxy radical (Fig. 2). Irradiation of oxygen-free basic solutions of phenol II did not produce detectable amounts of radical III.



However, in the dark, the addition of diazonium Ia to a aqueous solution of the phenol II gave a very strong e.s.r. signal of radical III at pH above 5. This oxidative power of the diazonium cation Ia was further demonstrated by its ability to generate in the dark the phenoxy radical of 2,6-di-*t*-butyl-4-methylphenol and the Wurster's Blue cation from tetramethyl-*p*-phenylenediamine in oxygen-free basic solutions. Radical III could not be detected in a basic aqueous solution of Ia standing at room temperature. This can be attributed to the rather slow rate of solvolysis of I and the rather short lifetime of the radical III. The chemical oxidation by the diazonium cation Ia of the phenol II presumably occurs through the phenolate anion.

The formation of radical III by oxidation of II by Ia implies the presence of another paramagnetic species resulting from the one-electron reduction of the diazonium cation Ia. Radicals of this type have been proposed as intermediates in the electrolysis of aqueous solutions of diazonium salts.<sup>10</sup> However, present attempts at electrolysis of aqueous solutions of Ia at various pH values failed to yield detectable amounts of any paramagnetic species.

Although, in basic aqueous solutions, diazonium cations can exist in equilibrium with the corresponding

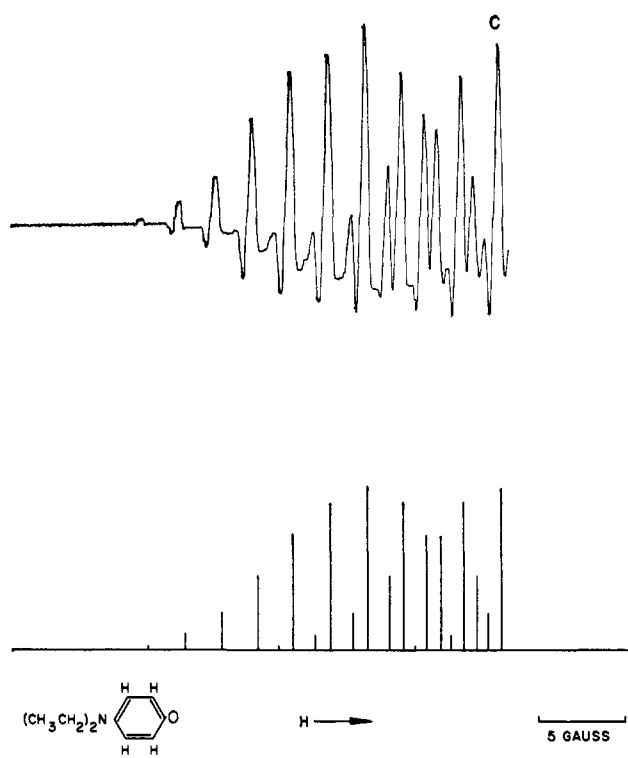


Fig. 2.—Second derivative of the electron spin resonance absorption spectrum of irradiated solutions of *p*-diethylaminobenzenediazonium chloride. Reconstruction for  $a_N = 7.45$ ,  $a_{CH} = 2.08$ , and  $a_{CH_2} = 4.16$  gauss; C = center.

diazotate anion, the work of Lewis and Suhr<sup>11</sup> establishes that the constant  $K$ , defined below, is very large for aryls containing electron-donating substituents. Their work indicates that the value of  $K$  for compound



$$K = (\text{ArN}_2^+)(\text{OH}^-)^2 / \text{ArN}_2\text{O}^-$$

Ia is greater than  $10^7$ , from which it follows that for a concentration of  $\text{ArN}_2^+ = 1 M$  and at pH less than 12 the diazotate ion concentration is less than  $10^{-10} M$ . In addition, the other hypothesized species, the diazoic acid, is sufficiently acidic to prevent it having a concentration greater than the diazotate ion in basic solutions. This argument indicates that, under the conditions discussed, neither of these species plays a part in the photochemistry of either Ia or Ib. The above arguments and observation show that the generation of *p*-dialkylaminophenoxy radicals on photolysis of aqueous solutions of the corresponding diazonium salts Ia and Ib arises from a secondary reaction of the photolysis product, previously established as being II,<sup>12</sup> and starting material and has nothing to do with the basic photochemistry of the system. It is evident that the observations of Boudreaux<sup>5</sup> do not require the formation of aryl radicals. The usual reaction of diazonium salts with phenolate ions gives azo dyes.<sup>13</sup> As has been shown, oxidation is another possible reaction. Preliminary studies show that in the systems studied at least 20% of the diazonium salt Ia is converted on photolysis to radical III.

(11) E. S. Lewis and H. Suhr, *Chem. Ber.*, **91**, 2350 (1958).

(12) J. DeJonge and R. Dijkstra, *Rec. trav. chim.*, **68**, 426 (1948).

(13) (a) Z. J. Allan, *Collection Czech. Chem. Commun.*, **16**, 620 (1951);  
(b) H. Zollinger, *Helv. Chim. Acta*, **36**, 1070 (1953).

(10) J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 3208 (1955).

**Electron Spin Resonance Spectra.**—The second derivatives of the observed electron spin resonance absorption spectra are shown in Fig. 1 and 2. Because of the length of the spectra, only the low-field half is given. The spectra have been reconstructed using the coupling constants in Table I and assuming the phenoxy structure. The reconstructions match the experimental spectra in all details. Special care was

TABLE I  
COUPLING CONSTANTS FOR THE DIALKYLAMINOPHENOXY

RADICALS IN AQUEOUS SOLUTION (GAUSS)			
R = CH <sub>3</sub>	R = C <sub>2</sub> H <sub>5</sub>		
N	7.45	N	7.45
CH	2.14	CH	2.08
CH <sub>3</sub>	7.08	CH <sub>2</sub>	4.16

taken to obtain the tails of the spectra in order to measure the smaller ring proton coupling constants. In the case of the diethyl radical, one cannot distinguish between the ring proton and the CH<sub>2</sub> proton coupling constants. The analogy with the dimethyl radical, however, suggests the order given in Table I, since the nitrogen and ring proton coupling constants should not be much different in the two radicals. Some interesting properties of the spectra of these radicals may be mentioned. In the first place, one observes (Table I) a much smaller spin density at the ethyl CH<sub>2</sub> proton in the *p*-diethylaminophenoxy than at the methyl CH<sub>3</sub> protons in the *p*-dimethylaminophenoxy. This discrepancy can be explained in terms of hyperconjugation. A discussion of hyperconjugation of the (CH<sub>3</sub>)<sub>2</sub>-C- and (CH<sub>3</sub>)<sub>2</sub>-N- groups using the valence bond model was given by McLachlan.<sup>14</sup> In this model, steric hin-

(14) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); J. R. Bolton, A. Carington, and A. D. McLachlan, *ibid.*, **5**, 31 (1962).

drance with respect to free rotation of the alkyl group can lead to a lower average spin density on the alkyl. The present results give a direct measure of the average exchange integral between the nitrogen p<sub>z</sub> and the C-H orbital. Any inductive effect on the spin distribution has to be very small since in both radicals the nitrogen and ring coupling constants remain the same. In the diethylaminophenoxy radical the hyperfine lines are broadened, presumably due to the small unresolved hyperfine splitting of the CH<sub>3</sub> protons. Secondly, it was found that the spectra are solvent dependent.

Although a more detailed discussion on the solvent effects will be given at a later date, some results will be mentioned presently. In water solutions, the four ring-proton coupling constants are the same, a somewhat accidental result in view of the symmetry of these radicals. It is interesting that addition of dimethyl sulfoxide (DMSO) leads to a change in coupling constants. The ring-proton coupling constants are no longer the same and occur in two pairs in DMSO solution (see Table II). Preliminary calculations have shown that the spectral changes can be explained in the same fashion as was done by Gendell, Freed, and Fraenkel for semiquinones.<sup>1</sup> The electron cloud is polarized by the solvent, leading to these effects.

TABLE II  
SOLVENT EFFECT ON COUPLING CONSTANTS OF  
*p*-DIMETHYLAMINOPHENOXY RADICAL

Solvent composition, %	Dimethyl sulfoxide	Coupling constants (gauss)			
		N	CH(2x)	CH(2x)	CH <sub>3</sub>
100	0	7.45	2.14	2.14	7.08
50	50	7.05	2.52	1.65	6.64
0	100	6.29	3.53	0.81	5.90

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## Electrophilic Displacement Reactions. XVI. Metal Ion Catalysis in the Protodeboronation of Areneboronic Acids<sup>1-3</sup>

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A kinetic investigation has been made of the protodeboronation of benzeneboronic acids, and the effects of pH and of substituents in the *o*-, *m*-, and *p*-positions on rate. The pH-rate profile shows a base-catalyzed and an "uncatalyzed" reaction, each of which is catalyzed by cadmium ion in turn. The *ortho-para* ratios generally parallel those observed earlier for the reaction in the absence of cadmium ion, but the *meta*- and *para*-substituted acids show different linear free energy relationships for the two kinds of reaction. Salts of magnesium, zinc, copper(II), lead(II), nickel(II), cobalt(II), and silver also catalyze the protodeboronation. The mechanism of the metal ion catalyzed protodeboronation is discussed in the light of the experimental results.

Previous investigations on protodeboronation of benzeneboronic acids have revealed the existence of three mechanisms which can be distinguished on the

(1) (a) Presented in part at the Symposium on Organometallic Compounds, sponsored by the Inorganic Chemistry Division of the Chemical Institute of Canada and the University of British Columbia, Vancouver, B. C., Sept. 5, 1962; (b) preceding paper in this series: H. G. Kuivila, J. F. Reuwer, Jr., and J. A. Mangravite, *Can. J. Chem.*, **41**, 3081 (1963).

(2) Taken in part from the Ph.D. Dissertation of J. F. R., Jr., University of New Hampshire, June, 1962.

(3) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Contract AF 49 (638)-312 and by the Atomic Energy Commission under contract AT (30-1)-2970.

basis of kinetics. One of these is a general acid catalyzed reaction in which the rate-determining step involves proton transfer from an acid to the carbon of the benzene ring bearing the dihydroxyboron group.<sup>4</sup> The rates for *m*- and *p*-substituted benzeneboronic acids are correlated by  $\sigma^+$  with a  $\rho$ -value of  $-5.0$ . A second mechanism displays specific hydroxide ion catalysis below pH 6.8 and is believed to involve proton transfer from a water molecule to the benzeneboronate

(4) H. G. Kuivila and K. V. Nahabedian, *J. Am. Chem. Soc.*, **83**, 2159, 2164 (1961); K. V. Nahabedian and H. G. Kuivila, *ibid.*, **83**, 2167 (1961).