experimental value of V_s and V_l, the predicted volume expansion (or contraction), ΔV_m, on melting has to fit the experimental values exactly (Table I, ΔV_m).

In part 2 of this theory we shall give a new and complete partition function for the liquid state and compare it to the SST partition function; discuss the potential function for liquids under extreme pressures ($>5 \times 10^3$ atm), at constant temperature,[19] and at constant high pressure;[20] and derive equations for the kinetic[21] and potential energy for molecules in a liquid surface.

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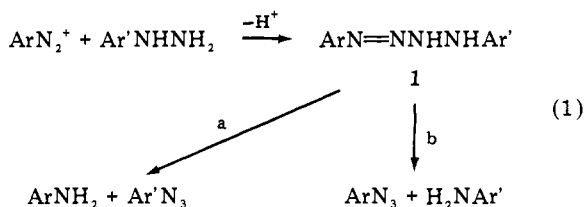(21) L. S. Levitt, *Bull. Am. Phys. Soc.*, **II-3**, 339 (1958).

An Investigation of the Reduction of Aryldiazonium Ions by Hydrazines

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Abstract: Reaction of acetonitrile solutions of aryldiazonium fluoroborates with arylhydrazines leads to reduction of the diazonium ion. This reaction generates arenes and protonated hydrazobenzenes showing nuclear polarization (CIDNP). An analysis of the nuclear polarizations leads to the conclusion that the reaction proceeds via an initial electron transfer from hydrazine to the diazonium ion to generate a radical pair consisting of a diazenium radical, **5**, and an aryldiazenyl radical, **9**. Loss of nitrogen from **9** produces an aryl radical paired with **5**. This radical pair is responsible for nuclear polarization. When the reducing agent is phenylhydrazine, radical **5** is further oxidized to generate polarized benzene. Reaction of *p*-nitrobenzenediazonium fluoroborate with *p*-nitrophenylhydrazine produces an immediate precipitate which has been characterized as 1,4-bis(*p*-nitrophenyl)tetrazene (**10**).

One of the more interesting reactions of aryldiazonium ions is that with arylhydrazines to produce arylazides and anilines (eq 1).[1] This reaction, which takes place in strong
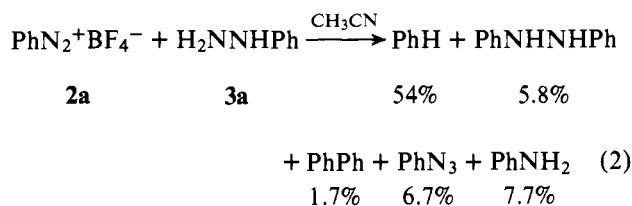
$$ArN_2^+ + Ar'NHNH_2 \xrightarrow{-H^+} ArN{=}NNHNHAr'$$

1

$$ArNH_2 + Ar'N_3 \qquad ArN_3 + H_2NAr' \qquad (1)$$

(paths a and b)

aqueous acid solution, is thought to involve heterolytic cleavage of an intermediate 1,4-diaryltetrazene, **1**.[2] Inasmuch as hydrazines are known to be effective reducing agents,[3] it was of interest to us to investigate the reaction of hydrazines with diazonium salts under conditions in which the reaction shown in eq 1 may be supplanted by a reduction of the diazonium ion.
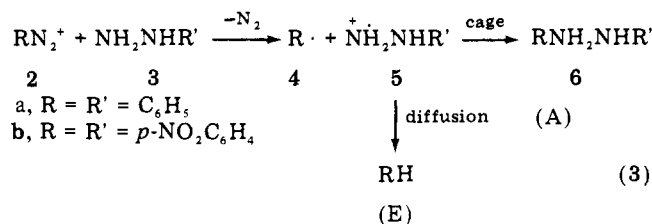
Results and Discussion

The reaction shown in eq 1 undoubtedly proceeds via an ionic mechanism whereas reductions of diazonium ions usually involve free-radical intermediates.[4] Hence, it seemed that a less polar solvent and the absence of acid might favor reduction. That this is the case is demonstrated by the reaction of ben-

zenediazonium fluoroborate (**2a**) and phenylhydrazine (**3a**) in acetonitrile solution which gives the products shown in eq 2.

$$PhN_2^+BF_4^- + H_2NNHPh \xrightarrow{CH_3CN} PhH + PhNHNHPh$$

| **2a** | **3a** | 54% | 5.8% |

$$+ PhPh + PhN_3 + PhNH_2 \qquad (2)$$

| 1.7% | 6.7% | 7.7% |

Having observed that hydrazines can reduce diazonium salts, we have carried out a number of experiments designed to elucidate the mechanism of this interesting reaction. In many cases, reactions leading to the reduction of diazonium ions involve radical pairs and generate products showing nuclear polarization (CIDNP)[5] when carried out in the probe of an NMR spectrometer.[6] Accordingly, we have carried out the reaction shown in eq 2 in the probe of ^{13}C and ^1H NMR spectrometers. These experiments resulted in the observation of strong emissions (E) for the protons and carbon-13 atoms of benzene. In addition, the ^{13}C spectrum showed two enhanced absorptions (A) at δ 130.9 and 140.9 ppm. It was found that these enhanced absorptions corresponded to C_1 and C_3 of hydrazobenzene to which an excess of HBF_4 had been

added. The observation and identification of nuclear polarization in these systems allow us to postulate that the reaction proceeds via a radical pair consisting of phenyl radical, **4a**, and the diazenium radical cation **5a**. This radical pair reacts in the manner shown in eq 3. If one assumes that the nitrogen-cen-
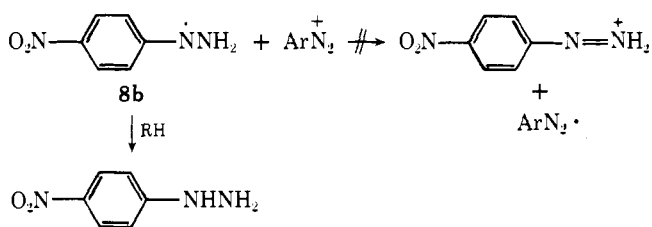
$$RN_2^+ + NH_2NHR' \xrightarrow{-N_2} R\cdot + \overset{+}{N}H_2NHR' \xrightarrow{cage} RNH_2NHR'$$

$$\begin{array}{ccccccc} \textbf{2} & & \textbf{3} & & \textbf{4} & \textbf{5} & & \textbf{6} \end{array}$$

a, $R = R' = C_6H_5$
b, $R = R' = p\text{-}NO_2C_6H_4$ $\qquad \Big\downarrow \text{diffusion} \qquad$ (A)

$$RH \qquad\qquad (3)$$

(E)

tered radical **5** has the higher g value of the pair[7] and uses the known values of hyperfine splittings in aryl radicals, Kaptein's rules[8] may be employed to predict the sign of the nuclear polarization ($\Gamma = \mu\epsilon\Delta gA$). Thus, an arene produced by diffusion from the cage and subsequent hydrogen abstraction will exhibit emission signals for its protons ($---+ = - = E$) and the majority of its carbons. Likewise, enhanced absorptions are expected for C_1 and C_3 of the cage recombination product, a protonated hydrazobenzene, **6** ($-+-+ = A$).

Reaction of p-nitrobenzenediazonium fluoroborate (**2b**) with phenylhydrazine (**3a**) produced the striking CIDNP result shown in Figure 1. In addition to polarized nitrobenzene, emissions were observed for the protons of benzene. An analysis of the reaction products showed that benzene was produced in 66.5% yield while nitrobenzene amounted to 33.6%.

In order to explain this interesting cross polarization, we propose that the phenylhydrazyl radical **8a** is further oxidized to produce phenyldiazene (**7**) as shown in Scheme I. We have previously shown that aryldiazenes decompose in a second-order reaction which is accompanied by nuclear emissions from the arenes produced.[6f] Thus, the benzene polarization in the reaction of **2b** with phenylhydrazine (**3a**) arises from the radical decomposition of an intermediate phenyldiazene. Aryldiazenes have previously been produced when hydrazines are oxidized with either cupric halides[9] or ferricyanide[10] and CIDNP signals from benzene have been reported in the oxidation of phenylhydrazine with p-benzoquinone.[11a,b]

The reaction of **2a** with p-nitrophenylhydrazine proceeds sluggishly at room temperature and polarized benzene is observed only at elevated temperatures (150 °C). It is interesting that no polarized nitrobenzene can be observed in the system. The absence of polarized nitrobenzene in this reaction may be explained by the effect of the electron-withdrawing nitro group, which lowers the reduction potential of the p-nitrohydrazyl radical (**8b**) relative to that of the phenylhydrazyl radical

$$O_2N\text{---}\langle\!\!\!\bigcirc\!\!\!\rangle\text{---}\overset{\cdot}{N}NH_2 + Ar\overset{+}{N}_2 \ \#\!\!\!\to\ O_2N\text{---}\langle\!\!\!\bigcirc\!\!\!\rangle\text{---}N{=}\overset{+}{N}H_2$$

$$\textbf{8b} \qquad\qquad\qquad\qquad\qquad\qquad +$$

$$\Big\downarrow RH \qquad\qquad\qquad\qquad\qquad Ar\overset{\cdot}{N}_2\cdot$$

$$O_2N\text{---}\langle\!\!\!\bigcirc\!\!\!\rangle\text{---}NHNH_2$$

(**8a**).[12] Thus, **8b** simply abstracts hydrogen rather than undergoing extensive further oxidation.

These results show that radical pair $\overline{4 + 5}$ is involved in the reduction of diazonium ions by hydrazines. The fact that the hydrazine is also oxidized raises the possibility that the short-chain mechanism shown in eq 4–7 is involved. In this
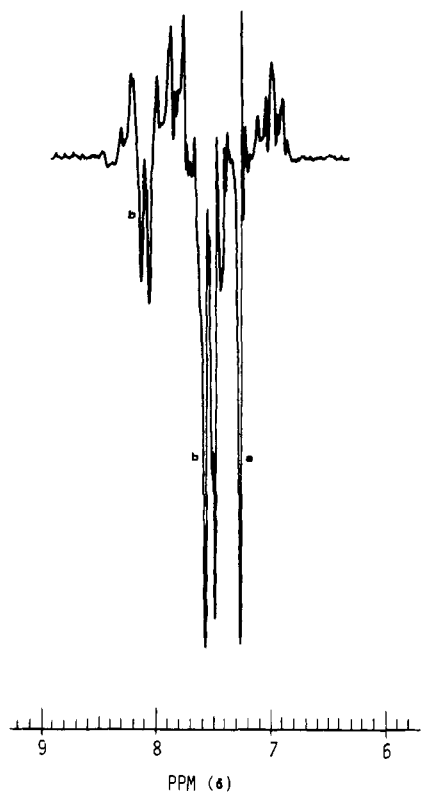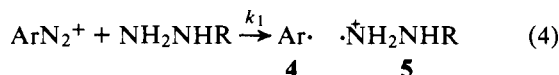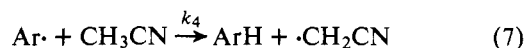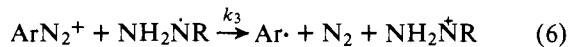
$$ArN_2^+ + NH_2NHR \xrightarrow{k_1} Ar\cdot \quad \cdot\overset{+}{N}H_2NHR \qquad (4)$$

$$\begin{array}{ccc} & \textbf{4} & \textbf{5} \end{array}$$

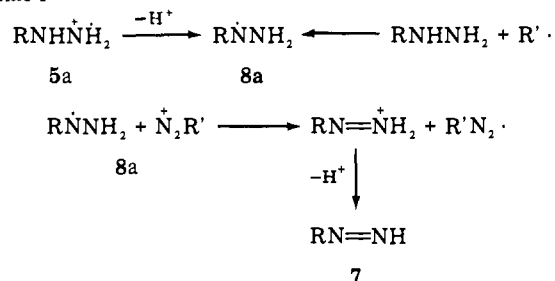$$Ar\cdot + NH_2NHR \xrightarrow{k_2} ArH + NH_2\overset{\cdot}{N}R \qquad (5)$$

Figure 1. ^{1}H NMR spectrum recorded during the reduction of p-nitrobenzenediazonium tetrafluoroborate (**2b**) by phenylhydrazine (**3a**) showing emissions for benzene (a) and nitrobenzene (b).

Scheme I

$$RNH\overset{\cdot}{N}H_2 \xrightarrow{-H^+} R\overset{\cdot}{N}NH_2 \longleftarrow RNHNH_2 + R'\cdot$$

$$\textbf{5a} \qquad\qquad \textbf{8a}$$

$$R\overset{\cdot}{N}NH_2 + \overset{+}{N}_2R' \longrightarrow RN{=}\overset{+}{N}H_2 + R'N_2\cdot$$

$$\textbf{8a} \qquad\qquad\qquad\qquad -H^+\Big\downarrow$$

$$RN{=}NH$$

$$\textbf{7}$$

$$ArN_2^+ + NH_2\overset{\cdot}{N}R \xrightarrow{k_3} Ar\cdot + N_2 + NH_2\overset{+}{N}R \qquad (6)$$

$$Ar\cdot + CH_3CN \xrightarrow{k_4} ArH + \cdot CH_2CN \qquad (7)$$

sequence, the CIDNP results from the initiation step in eq 4 and the chain is carried in eq 5 and 6 with the major chain-terminating step being the reaction of aryl radicals with solvent (eq 7). The chain-propagating steps in this mechanism will lead to an arene which is not polarized and will serve to attenuate the arene emission. This fact is demonstrated by considering the expression for the initial intensity of arene emission (I) shown in the equation

$$I = c\frac{d[ArH_p]}{dt} - \frac{d[ArH]}{dt} \qquad (8)$$

where ArH_p is polarized arene. When one uses the steady-state approximation to obtain the rates of formation of polarized and unpolarized arene, the initial intensity is given by the equation

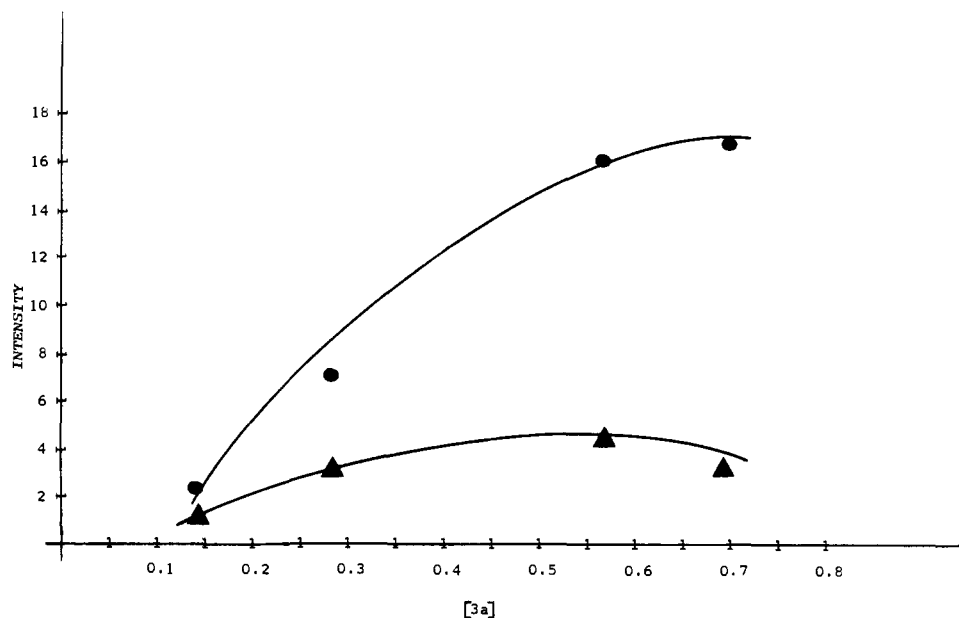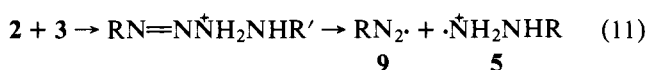$$I = [ArN_2^+][RNHNH_2](C' - k_1) - \frac{k_1k_2[RNHNH_2]}{k_4[CH_3CN]} \qquad (9)$$
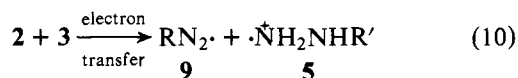
Figure 2. Plot of intensity of signals as a function of the concentration of phenylhydrazine for the reduction of diazonium salts: ●, benzenediazonium tetrafluoroborate (**2a**); ▲, *p*-nitrobenzenediazonium tetrafluoroborate (**2b**).

In the absence of a chain mechanism (only eq 4 and 7 operative), the intensity of CIDNP emission will be first order in hydrazine and diazonium ion. However, increasing the importance of the chain mechanism by increasing the hydrazine concentration will eventually attenuate the intensity of the CIDNP emission. Figure 2 shows CIDNP intensity as a function of the concentration of phenylhydrazine in the reduction of **2a** + **2b**. The attenuation of CIDNP intensity shown in Figure 2 provides evidence for the short-chain mechanism in eq 4-7.
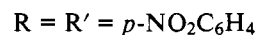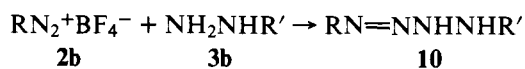
Since these experiments demonstrate that diazonium ions are reduced in a free-radical reaction involving the intermediacy of pair **4** + **5**, we may inquire as to the mechanism of the formation of this pair. The immediate precursor of pair **4** + **5** must be a pair consisting of the aryldiazenyl radical (**9**) and the aryldiazenium radical cation (**5**). Radical pair **5** + **9** can either be formed by a simple electron transfer (eq 10) or from an intermediate tetrazenium ion which undergoes homolytic cleavage (eq 11).

$$2 + 3 \xrightarrow[\text{transfer}]{\text{electron}} \underset{\mathbf{9}}{RN_2\cdot} + \underset{\mathbf{5}}{\cdot\overset{+}{N}H_2NHR'} \qquad (10)$$

$$2 + 3 \rightarrow RN{=}N\overset{+}{N}H_2NHR' \rightarrow \underset{\mathbf{9}}{RN_2\cdot} + \underset{\mathbf{5}}{\cdot\overset{+}{N}H_2NHR} \qquad (11)$$
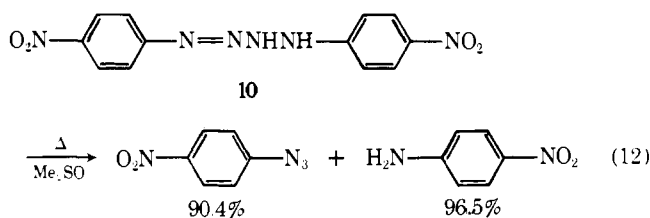
Equation 1 shows the postulated intermediacy of tetrazenes in the reaction of aryldiazonium ions with arylhydrazines to produce arylazides and amines. Clusius and Craubner[2] have used ^{15}N-labeled diazonium ion to demonstrate that cleavage of tetrazene by paths (a) and (b) (eq 1) occurs with equal probability. Thus, rapid prototropic rearrangement of the tetrazenium ion must precede cleavage. This rearrangement followed by homolytic cleavage could explain the cross polarization. However, in this investigation, we have succeeded in isolating 1,4-bis(*p*-nitrophenyl)tetrazene (**10**) and have shown that its decomposition does not generate polarized products.

The reaction of *p*-nitrobenzenediazonium fluoroborate (**2b**) with *p*-nitrophenylhydrazine (**3b**) in acetonitrile solution leads to the immediate formation of a precipitate in a reaction not accompanied by CIDNP. Elemental analysis and spectral data lead to the conclusion that the product of this reaction is

1,4-bis(*p*-nitrophenyl)tetrazene (**10**).

$$\underset{\mathbf{2b}}{RN_2{}^+BF_4{}^-} + \underset{\mathbf{3b}}{NH_2NHR'} \rightarrow \underset{\mathbf{10}}{RN{=}NNHNHR'}$$
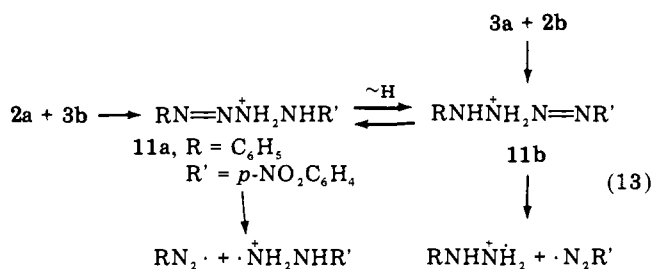
$$R = R' = p\text{-}NO_2C_6H_4$$

This conclusion is further confirmed by the fact that heating the compound in dimethyl sulfoxide solution results in near-quantitative yields of *p*-nitrophenyl azide and *p*-nitroaniline (eq 12). To our knowledge, this is the first example of the iso-

$$O_2N{-}\!\!\!\!\bigcirc\!\!\!\!-N{=}NNHNH{-}\!\!\!\!\bigcirc\!\!\!\!-NO_2$$

10

$$\xrightarrow[\text{Me}_2\text{SO}]{\Delta} O_2N{-}\!\!\!\!\bigcirc\!\!\!\!-N_3 + H_2N{-}\!\!\!\!\bigcirc\!\!\!\!-NO_2 \qquad (12)$$

$$90.4\% 96.5\%$$

lation of a 1,4-diaryltetrazene in the reaction of an aryldiazonium ion with an arylhydrazine.[14]

Although nuclear polarization is not detected in the reaction of **2b** with **3b** at room temperature, strong emission signals for the protons of nitrobenzene are observed when these reactants are mixed at 150 °C in dimethyl sulfoxide solution. In order to determine if the tetrazene **10** is an intermediate in the process leading to CIDNP in the reaction between **2b** and **3b**, **10** was heated in Me₂SO solution under conditions identical with those for which the CIDNP was observed. These experiments did not result in the detection of any nuclear polarization. Thus, it appears likely that tetrazene **10** is formed in a process which is competitive with radical pair formation but does not lead directly to pair **5** + **9**. This initial radical pair most probably results from the simple electron transfer shown in eq 10.

Cleavage of the tetrazenium ion to produce **5** + **9**, also appears unlikely when one considers the fate of the unsymmetric tetrazenium ions **11a** and **11b**. Equation 13 demonstrates that an equilibrium mixture of **11a** and **11b** can be approached from two directions and that both benzene and nitrobenzene should be polarized if **11a** and **11b** undergo homolytic cleavage. However, the experimental evidence indicates that reaction of **2b** with **3a** produces both polarized benzene and nitrobenzene but that reaction of **2a** with **3b** generates only polarized

$$3a + 2b$$
$$\downarrow$$
$$2a + 3b \longrightarrow RN{=}N\overset{+}{N}H_2NHR' \underset{\sim H}{\rightleftharpoons} RNH\overset{+}{N}H_2N{=}NR'$$
$$\textbf{11a, } R = C_6H_5 \qquad\qquad \textbf{11b}$$
$$R' = p\text{-}NO_2C_6H_4$$
$$\downarrow \qquad\qquad\qquad \downarrow \qquad (13)$$
$$RN_2\cdot + \cdot\overset{+}{N}H_2NHR' \qquad RNH\overset{+}{N}H_2 + \cdot N_2R'$$

benzene. These facts are not consistent with homolytic cleavage of tetrazenium ions as outlined in eq 13. Indeed, the mechanism in eq 13 would tend to favor the production of polarized nitrobenzene over benzene as the preferred cleavage would be that of **11b** which does not place the positive charge on the fragment bearing the electron-withdrawing nitro group.

Further evidence that electron transfer leads to pair $\overline{5 + 9}$ is obtained by examining the reaction in the presence of a competing electron acceptor. When **3a** is added to a solution of **2a** containing an equimolar amount of 3,5-dinitrobenzoic acid, the intensity of the benzene emission is reduced by a factor of 3.4 as compared to the reaction in the absence of the benzoic acid. Since 3,5-dinitrobenzoic acid is a good electron acceptor,[4] it is expected to compete with the diazo compound for the electron from the hydrazine. The effect of this competition is to reduce the concentration of radical pair $\overline{5 + 9}$ and diminish the intensity of the CIDNP signals. If the radical pair did not result from the electron transfer shown in eq 10, one would not expect such a dramatic effect on the CIDNP spectra when an electron acceptor is added.

Many mechanistic studies which have employed CIDNP suffer from the fact that they provide no information concerning the fraction of reaction proceeding by this pathway. However, in this study, we have shown that there are two distinct pathways for the reaction of hydrazines with diazonium ions, the ionic mechanism leading to azide and amine and the free-radical mechanism which produces arene and diarylhydrazine. It is difficult to imagine the production of arene by anything but a free-radical pathway. It is also unlikely that two different free-radical mechanisms are operative in this system. In the case of the reaction of **2a** with **3a**, 54% of the reaction produces benzene via the free-radical mechanism which we have elucidated using CIDNP techniques. Although it is true that only a small fraction of benzene is polarized, this is always the case in CIDNP investigations owing to the dynamics of spin selection. Additionally, in the present study, pair $\overline{5 + 9}$ may diffuse from the cage before loss of nitrogen from **5** precluding polarized products. However, these considerations do not negate the fact that radical pair $\overline{5 + 9}$ is crucial to the free-radical pathway.

We have carried out preliminary experiments in several other systems and have observed similar reductions accompanied by nuclear polarizations. Thus, reaction of *p*-methoxybenzenediazonium fluoroborate with phenylhydrazine produces benzene polarization. Likewise, **2a** is reduced by *p*-methoxyphenylhydrazine in a reaction which also produces polarized benzene. That the reaction is not limited to arylhydrazines is demonstrated by the fact that polarized benzene results from reaction of methylhydrazine with **2a**.

Conclusion

These experiments have demonstrated that diazonium salts can be effectively reduced by hydrazines under nonpolar conditions. The observation of products showing nuclear polarization leads to the conclusion that the reaction proceeds by a free-radical mechanism in which the first step is an electron transfer from the hydrazine to the diazonium ion.

Experimental Section

Materials. Commercial grade phenylhydrazine (**3a**) (Mallinckrodt) was used without further purification. Commercial grade *p*-nitrophenylhydrazine (**3b**) (Eastman) was used after recrystallization from ethanol. Aryldiazonium salts were prepared by standard methods[16] employing sodium nitrite for benzenediazonium fluoroborate (**2a**) and isoamyl nitrite for *p*-nitrobenzenediazonium tetrafluoroborate (**2b**). The fluoroborate salts were precipitated by the addition of 40% HBF_4.

Arylhydrazine Reduction of Aryldiazonium Salts. For ^1H NMR CIDNP spectra, **2a** (50 mg, 0.26 mmol) or **2b** (50 mg, 0.21 mmol) was dissolved in 0.4 mL of acetonitrile in a 5-mm NMR tube. An equimolar amount of phenylhydrazine **3a** was dissolved in 0.3 mL of acetonitrile and added. The spectra were then quickly recorded on a Varian EM 390 spectrometer. For the reaction with *p*-nitrophenylhydrazine, **3b** (40 mg, 0.26 mmol, or 32 mg, 0.21 mmol) was dissolved in 0.3 mL of dimethyl sulfoxide. Equimolar amounts of the aryldiazonium salts were also dissolved in dimethyl sulfoxide and the two solutions were mixed and then quickly placed in the NMR preheated to 150 °C. Spectra were then recorded.

Carbon-13 CIDNP was obtained by adding a mixture of phenylhydrazine (**3a**, 224 mg, 2.1 mmol) in 0.5 mL of acetonitrile to **2a** (400 mg, 2.1 mmol) or **2b** (497 mg, 2.1 mmol) in 1.5 mL of acetonitrile in a 10-mm NMR tube. The spectra were then recorded on a Varian CFT-20 spectrometer. In typical runs, one 20-μs pulse gave satisfactory signal to noise. Fourteen consecutive free induction decays (FIDs) were stored on a Sykes flexible disk recorder. The FIDs were Fourier transformed at the conclusion of the reaction and the spectra plotted. Each experiment was approximately 2 min in length.

A product analysis of the reaction mixture obtained from the phenylhydrazine reduction of **2a** (1.0 mmol), under the conditions of the CIDNP experiment, was carried out on a Du Pont 21-491 B Mass spectrometer, interfaced with a Varian Aerograph 2700 gas chromatograph equipped with a 5 ft 3% SE-30 on Variport 30, 100–125 mesh column, operating at 175 °C. The analysis revealed benzene (0.41 mmol, 54.5%), hydrazobenzene (0.024 mmol, 5.8%), biphenyl (0.0129 mmol, 1.7%), aniline (0.032 mmol, 7.7%), and phenyl azide (0.028 mmol, 6.7%).

An analysis for benzene and nitrobenzene in the reaction of phenylhydrazine with **2b** (0.21 mmol) was carried out on a Waters Associates high-pressure liquid chromatograph equipped with a μBondapak C-18 column using 60/40 CH_3CN–H_2O eluent at a flow rate of 2 mL min^{-1}. The results showed benzene (0.14 mmol, 66.5%) and nitrobenzene (0.071 mmol, 33.6%).

Preparation of 1,4-Bis(*p*-nitrophenyl)tetrazene (10). A solution of **2b** (3.0 g, 0.013 mmol) in 50 mL of CH_3CN was prepared. To this was added **3b** (1.95 g, 0.013 mmol) dissolved in 75 mL of CH_3CN. An orange precipitate was formed immediately. The precipitate was filtered with suction and recrystallized from ethanol. The dry precipitate melted at 55 °C with decomposition: IR (Fluorolube) 2123 (N=N) cm^{-1}; NMR (EtOH) δ 8.2 (d), 7.9 (d), 7.2 (d), 6.6 (d) ppm from Me_4Si; mass spectrum m/e 302. Anal. Calcd for $C_{12}H_{10}N_6O_4$: C, 47.7; H, 3.3; N, 27.8; O, 21.2. Found: C, 47.7; H, 3.4; N, 27.6; O, 21.4.

Decomposition of Tetrazene 10. Tetrazene **10** (26 mg, 0.086 mmol) was dissolved in 10 mL of CH_3CN; a 0.5-mL aliquot was then placed in an NMR tube and heated in an oil bath at 75 °C for 90 min. A product analysis was carried out on a Waters Associates high-pressure liquid chromatograph equipped with a μBondapak C-18 column using 50% CH_3CN–H_2O eluent at a flow rate of 1 mL min^{-1}. This analysis revealed *p*-nitrophenyl azide (0.078 mmol, 90.7%) and *p*-nitroaniline (0.083 mmol, 96.5%). When a solution of **10** (50 mg, 0.17 mmol) in 0.5 mL of dimethyl sulfoxide was heated to 150 °C in the probe of an NMR spectrometer, decomposition was not accompanied by nuclear polarization. A similar experiment in which **10** was heated in dimethyl sulfoxide containing excess HBF_4 did not result in the observation of CIDNP signals.

Effect of Phenylhydrazine Concentration on ^1H CIDNP Intensity. Four solutions of **3a** (0.14, 0.28, 0.56, and 0.69 M in CH_3CN) were prepared. Aliquots of 0.4 mL of **2a** (0.37 M) and **2b** (0.15 M) in CH_3CN were then reacted with **3a**. The spectra of each solution were recorded as soon as possible after addition and the intensity of the strongest emission peak was measured. The emission intensity in centimeters plotted as a function of the concentration of **3a** is shown in Figure 2.

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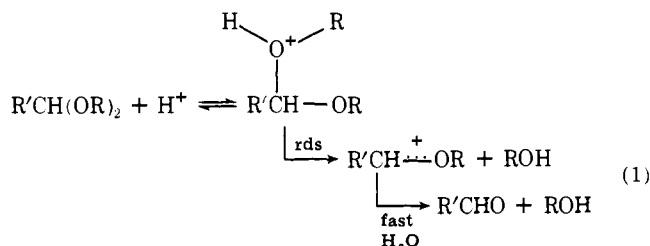(16) A. I. Vogel, "A Textbook of Practical Organic Chemistry", 3rd ed., Longman, London, 1957, p 590 ff.

Substituent Effects on the General- and Specific-Acid-Catalyzed Hydrolyses of Acetals of Benzaldehydes[1]

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Abstract: The effects of solvent and substituents on the general-acid-catalyzed (GAC) hydrolysis of acetals of benzaldehydes are defined. Contrary to earlier reports, GAC hydrolysis is important for a broad spectrum of benzaldehyde acetals. A variety of linear free energy relationship (LFER) cross correlations are established so that the Brønsted α may be calculated for nearly any acetal of any benzaldehyde. The smallest α measured is 0.70 for the hydrolysis of benzaldehyde trifluoroethyl ethyl acetal and the largest is defined as >0.9 for the hydrolysis of *m*-chlorobenzaldehyde diethyl acetal. Procedures for accurately measuring large α values are established. These results reemphasize the importance of defining α as opposed to use of the more ambiguous term specific acid catalysis. The mechanistic implications of LFER cross correlations are discussed in terms of Jencks–O'Ferrall diagrams. Evidence is summarized for rate-determining diffusional separation of the (carboxonium ion)·(conjugate base of the catalyzing acid)·(alcohol) aggregate.

The hydrolysis of acetals has received wide attention in recent years, culminating in two recent review articles.[2] Consensus of opinion appears to be that acetals hydrolyze by an A1 mechanism (eq 1) except in certain "special" cases.[2,3]

$$R'CH(OR)_2 + H^+ \rightleftharpoons R'CH{-}OR \;\; \overset{H\diagdown \atop O^+}{\underset{}{\diagup R}}$$

$$\xrightarrow{\text{rds}} R'CH{\overset{+}{=}}OR + ROH$$
$$\xrightarrow[\substack{\text{fast} \\ H_2O}]{} R'CHO + ROH \tag{1}$$

In previous communications it has been shown that, for R' = Ar, hemiacetals build up in solution to sizable concentrations (ca. 40% of the total substrate concentration, in some cases);[4] in this paper attention is focused on the chemistry occurring during the initial carboxonium ion forming portion of the reaction, as indicated by eq 1. In particular, data are presented to show that when R' = Ar and R = alkyl, the first two steps of eq 1 are merged and hydrolysis occurs by a "concerted catalysis" pathway.[5] Indeed, it now appears that acetals and

ketals hydrolyze in aqueous solution by this common pathway, although the rate-determining step may differ, depending on the nature of R' and R. This work supports the suggestion that diffusional separation of the (carboxonium ion)·(conjugate base of the acid catalyst)·(alcohol) aggregate may be rate determining[6,7] and suggests a proper function for Asp 52 in the active site of lysozyme.

Experimental Section

Materials. Reagent grade dioxane was refluxed over LiAlH₄ or sodium metal for several hours, distilled, and stored in brown bottles in the freezer until used. The variously substituted benzaldehydes, ethyl orthoformate, propargyl alcohol (propynol), 2,2,2-trifluoroethanol, 2-chloroethanol, and 2-methoxyethanol were the best grade available from Aldrich Chemical Co.

Diethyl acetals of benzaldehydes were synthesized by traditional methods. Diethyl and dimethyl acetals were conveniently prepared from the appropriate benzaldehyde, ethyl or methyl orthoformate, and a catalytic amount of toluenesulfonic acid.[8] Other dialkyl acetals (e.g., di-2-chloroethyl acetals) were conveniently prepared from the appropriate benzaldehyde, alcohol (e.g., 2-chloroethanol), and a catalytic amount of toluenesulfonic acid in benzene (the water formed as the reaction proceeds was removed azeotropically using a Dean-Stark trap).[9]