The Quasi-Solid Liquid Lattice and Volume Change on Melting of a Solid. A Modified Significant Structure Theory of Liquids. 1

Leonard S. Levitt* and Eric T. Hsieh

Contribution from the Department of Chemistry, College of Science, The University of Texas at El Paso, El Paso, Texas 79968. *Received August 30, 1978*

Abstract: A modification of the significant structure theory of liquids (SST) is made, in which it is assumed that a change of coordination number occurs when a solid melts. On this basis, a "hole" factor (χ) and a coordination factor (κ) are derived, using Lindemann's theory of melting and the molar refractions of solid and liquid. From the calculations of κ, it is concluded that every solid lattice should, theoretically, contract on melting, and this factor therefore represents a negative term in the volume change. On the other hand, the calculated χ factors represent a positive term, and the net volume change is due to the combination of these two opposing factors. It is found that κ and χ are related by $\kappa = V_l/V_s\,(1 + \chi)$, from which the change in volume on melting, ΔV_m, is given by $\Delta V_m = \kappa V_s\,(1 + \chi - 1/\kappa)$.

Introduction

A simple theory of the liquid state which has received considerable attention during the past 2 decades is the "significant structure theory" (SST) of Eyring and his collaborators.[1-7] This theory approaches the liquid from the second boundary of the liquid state—the solid-liquid boundary. The structural model is based on the melting process of the solid, and suggests that the liquid inherits, more or less, most of the solid lattice structure. This may seem unreasonable, but it works amazingly well in predicting the thermodynamic properties of a considerable number of liquids over an extensive range of temperature and pressure.[8-11] Above all, this theory offers a great deal of insight into the nature of the liquid state.

The SST structural model was set up on the basis of the following considerations and experimental facts: (a) For a normal phase transition from solid to liquid, there is always an expansion in volume. (Water is considered an exception.) (b) At the triple point the vapor pressure of both solid and liquid state is the same. (That is, there are no additional molecules escaping to the vapor phase upon melting.) (c) X-ray diffraction studies[12] have shown that the intermolecular spacing (time average) among nearest neighbors in a liquid is similar to that found in the solid. The long-range order in the solid, however, disappears in the liquid, but there still is some short-range order remaining, which, upon increasing the temperature, gradually disappears.

Significant Structures[1-7]

The basic idea of SST is that those structures which are considered to make the major contribution to the thermodynamic properties of the liquid system are singled out and any others are ignored. In this model, three significant structures are considered: (a) *the solid-like degrees of freedom:* possessed by molecules having only other molecules as nearest neighbors (Their positions are restrained in a manner similar to their situation in the solid lattice.); (b) *the gas-like degrees of freedom:* possessed by molecules having a vacancy (or vacancies) as nearest neighbors (They will have three-dimensional translational degrees of freedom by virtue of their ability to move into the neighboring hole(s).); (c) *positional degeneracy of solid-like molecules:* because of the existence of molecular size holes, a solid-like molecule will have a positional degeneracy other than its most stable equilibrium lattice position. This positional degeneracy is proportional to the number of the neighboring holes which exist, and inversely proportional to the energy required to preempt the neighboring hole from the competing neighboring molecules.

Under the assumption that the liquid state will maintain the same lattice structure (same unit cell) as that of the solid state, letting V_l and V_s represent the molar volume of liquid and solid, respectively, the following relations were obtained. The total volume of holes = $V_h = (V_l - V_s)$, where the V's are molar volumes. Since the holes are of molecular size, the mole fraction of holes should be $V_h/V_s = (V_l - V_s)/V_s$. According to the definitions of solid-like molecules and gas-like molecules, the mole fraction of solid-like molecules is V_s/V_l, which is also the probability of a molecule having only other molecules as nearest neighbors. The mole fraction of gas-like holes is $V_h/V_l = (V_l - V_s)/V_l$, which also equals the mole fraction of gas-like molecules because V_h/V_l is the probability of a molecule having vacancies as nearest neighbors. If n_h be the number of equilibrium sites accessible to a solid-like molecule in addition to its single most stable position, then $n_h = z(V_l - V_s)/V_l$ where z is the coordination number (number of nearest-neighbor sites). But n_h should be proportional to the mole fraction of holes, so $n_h = n(V_l - V_s)/V_s$ where n is a proportionality constant. Combining the last two equations to eliminate n_h, $n = zV_s/V_l$, which means n is the number of nearest neighboring sites occupied by molecules (not holes). Then $n_h + n = z$.

The Melting Process

At the melting point, a certain large number of molecules will have a large enough kinetic energy to overcome the local potential energy. The result is that they vibrate too vigorously and their positions deviate too far from the lattice site, thus causing a large number of "empty sites". Eyring and his collaborators called this phenomenon" liftoff", and these lifted-off molecules are considered as still remaining in the dense phase. But because of the existence of these molecules and the large number of empty sites (which are considered as holes of molecular size), the original solid lattice equilibrium is broken. The holes, the lifted-off molecules, and the remaining solid-like molecules seek a new equilibrium, which is the liquid lattice. Eyring and co-workers proposed that this liquid lattice would have the same coordination sphere (the same unit cell with the same cell volume, and the same number of lattice sites per cell), since the intermolecular spacing is approximately the same in both states. The lattice sites are then occupied by molecules and molecular-size holes. This lattice structure explains the short-range order found in a liquid. The introduction of molecular-size holes into the lattice explains the disappearance of the long-range order and the fluidity of the liquid, as well as the volume expansion. The net volume expansion upon melting is explained by the additional empty sites (the molecular-size holes) introduced into the system.

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According to Lindemann,[13-15] as the temperature of a solid increases, the molecules vibrate more vigorously, and some molecules will attain a vibrational amplitude equal to or larger than one-half of the intermolecular spacing. At temperatures below the melting point, these molecules are responsible for diffusion in a solid system. At the melting point, T_m, the mole fraction of high-energy molecules is approximately $e^{-\theta_m/T_m}$. This is the maximum fraction for which a solid system can still maintain its rigidity, but $\theta_m = h\nu_m/k$ and ν_m is given by Lindemann as

$$\nu_m = 2.80 \times 10^{12} \left(\frac{T_m}{MV_m^{2/3}}\right)^{1/2} = 2.8 \times 10^{12} \left(\frac{T_m d_m^{2/3}}{M^{5/3}}\right)^{1/2} \tag{1}$$

where M is the molecular weight, V_m is the molar volume of solid at the melting point, d_m is the corresponding density, and ν_m is the characteristic frequency corresponding to the vibrational amplitude equal to one-half of the lattice spacing in the solid at T_m. The heat of fusion, then, is the molar activation energy which causes melting, when the fraction of high-energy molecules becomes greater than the limit, which is $\sim e^{-\theta_m/T_m}$.

An important point is that the total *kinetic* energy of the solid and liquid is the same at the same temperature. Lindemann[9] explained the positional instability of these molecules as being due to the large vibrational amplitude, which will cause an overlap of the vibrations of neighboring molecules and a sharing of their E_k. As a result of this, one of the two molecules will have enough kinetic energy to leave its lattice site and become "free" in the solid. Below the melting point, the number of these "free" molecules must be less than the number of the empty sites in the solid system, and the migration (diffusion) rate can satisfy the time limit to relax the local instability. At T_m, the diffusion rate (which is dependent on the number of empty sites in the solid) is barely able to relax the instability caused by the large number of "free" molecules. As more energy is introduced into the solid system, the solid molecules redistribute themselves into higher vibrational energy levels, and thus more "free" molecules are produced so rapidly that it requires a faster rate to relax the local instability than the diffusion rate. Thus we get additional "lifted off" molecules for which there are no more empty sites to migrate to, and this causes the disruption of the solid lattice structure. These additional lifted off molecules will still stay in the dense phase because the vapor pressure at T_m (actually, the triple point) for both the solid and liquid is almost the same. The result is that additional holes are created in the dense phase (liquid).

The problem remaining is what is the mole fraction of the "extra" holes which are introduced into the liquid system upon melting. If we assume that the vibrational frequency (whose corresponding vibrational amplitude, A, equals the intermolecular spacing in the solid) is ν_A, then we might assume that $\nu_A = 2\nu_m$, and if $\theta_A = h\nu_A/k$, then $E_A = 2E_m$. Molecules having vibrational amplitude A can lift off without sharing the kinetic energy of their neighbors. But molecules with vibrational frequency between θ_m and θ_A need to share a neighbor's kinetic energy to lift off. For these molecules, therefore, a factor of ½ should be introduced into the calculation of the number of "lifted-off" molecules due to melting of the solid. Assume that ΔH_m can raise the solid temperature to T', without melting it; then the total number, N_{ex}, of "extra" new holes formed in the liquid phase is

$$\begin{aligned} N_{ex} &= N_0 \left[e^{-\theta_A/T'} + \frac{1}{2}\left(e^{-\theta_m/RT'} - e^{-\theta_A/T'}\right)\right] \\ &= \frac{N_0}{2}\left(e^{-\theta_m/T'} + e^{-\theta_A/T'}\right) \end{aligned} \tag{2}$$

and T' is given by

$$T' = T_m + \Delta H_m / C_{p(m)} \tag{3}$$

where $C_{p(m)}$ is the heat capacity of the solid at T_m and constant pressure. The total number of holes in the liquid state at the melting point is therefore

$$N_h = \frac{N_0}{2}\left(e^{-\theta_m/T'} + e^{-2\theta_m/T'}\right) \tag{4}$$

since, before melting, the number of holes ($\ll 10^{-5}$ mole fraction)[16] is negligible.

Liquid Structure in the Low-Temperature Region—a "Quasi-Lattice Structure"

The liquid theory for the low-temperature region actually is a modified SST. At the triple point the vapor pressure, and therefore the number of molecules escaping from the dense phase to the vapor phase, is the same for both the solid and liquid. This suggests that, at temperatures not too far from the melting point, the liquid phase has about the same magnitude of intermolecular potentials as does the solid, but a little smaller.

In accord with SST, we still define the significant structures in a low-temperature liquid as (a) solid-like degrees of freedom; (b) gas-like degrees of freedom; (c) positional degeneracy of solid-like molecules. The definition of each term still remains the same. The main difference in this theory is that we do *not* assume that the coordination number remains unchanged upon melting. The volume change due to the change in coordination number will be calculated. We call this factor the coordination factor, κ. In SST, the volume change is explained solely on the basis of the formation of holes upon melting. Here, we take this part as the χ factor. By using these two factors, we can explain the volume change of the solid on melting.

The Coordination Factor κ

In the following discussion, we neglect the number of empty sites formed in the interior of the solid at very low temperature, without a corresponding loss of molecules into the vapor phase.

The total molar volume of a solid crystal can be analyzed into two parts:

$$V_s = R_m(s) + \delta_s \tag{5}$$

where $R_m(s)$ is the molar refraction, given by

$$R_m(s) = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)_s \frac{M}{d_s} \tag{6}$$

which is the actual volume occupied by 1 mol of the solid-phase molecules. The subscript "s" refers to solid, n_D is the index of refraction, d is the density, M is the molecular weight, and δ_s is the molar "dead space" of the solid, which is the "frozen in" empty space between the lattice points. This empty space does not include the solid-state empty lattice sites because empty sites can be occupied through diffusion, but δ_s cannot be utilized for diffusion. As molecules sublime into the vapor phase, the empty sites left behind are considered molecular-sized holes.

Similarly, the molar liquid volume, V_l, can also be divided into the following three parts:

$$V_l = R_m(l) + \delta_l + V_{h(x)} \tag{7}$$

where $V_{h(x)}$ represents the volume of "extra" holes formed upon melting, and

$$R_m(l) = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)_l \frac{M}{d_l} \tag{8}$$

Since R_m is the molar volume actually occupied by molecules[17]

$$R_m(s) = R_m(l) = R_m(g) = R_m \tag{9}$$

At the melting point, there are high kinetic energy dense-phase molecules escaping to the vapor phase, and a corresponding number of empty sites left in the dense phase. This kind of empty site is actually included in the R_m term. It should be noted that $V_{h(x)}$ does not include these holes. As a matter of fact, the mole fraction of these holes in the solid phase at T_m has a numerical value[16] of 10^{-15}–10^{-9}, which is negligible by comparison.

According to SST, $\delta_s = \delta_l$, and therefore $V_l - V_s = V_{h(x)}$. In our modified theory, however, we assume that this fundamental simple relation of SS theory need be refined. Instead we assume that there is a difference, $\Delta\delta$, in the dead space of the solid lattice and that of the liquid quasi-lattice. On the basis of eq 5 and 9 we have

$$\Delta V_m = (V_l - V_s) = (R_m(l) + \delta_l + V_{h(x)} - (R_m(s) + \delta_s) \tag{10a}$$

and therefore

$$\Delta V_m = V_{h(x)} + (\delta_l - \delta_s) + R_m(l) - R_m(s) = V_h + \Delta\delta \tag{10b}$$

where ΔV_m is the actual change in molar volume on melting, $\Delta\delta = \delta_l - \delta_s$, and $R_m(l) = R_m(s)$. This $\Delta\delta$ term is obviously caused by the change in coordination (the mode of packing). By rearranging eq 10 one obtains

$$V_{h(x)} = \Delta V_m - \Delta\delta = V_l - (V_s + \Delta\delta) \tag{11}$$

and defining $\kappa V_s = (V_s + \Delta\delta)$, we have

$$\kappa = 1 + \Delta\delta / V_s \tag{12}$$

Here, κ is our coordination factor. Obviously, we see that κV_s represents the molar volume of a new coordinated solid which will have a different amount of "dead space" caused by a different mode of packing. It should be noted that this coordination *factor*, κ, reveals only the ratio of the number of nearest-neighbor lattice sites of the two differently packed lattices, whereas the coordination *number* is defined as the number of nearest-neighbor molecules, which can be less than the number of nearest-neighbor sites, because some of the latter can be empty. Thus, κV_s means the molar volume of molecules if they are packed in accord with the *liquid* quasi-lattice. From eq 11 and 5, we have

$$\kappa V_s = V_s + \delta_l - \delta_s = R_m + \delta_s + \delta_l - \delta_s = R_m + \delta_l \tag{13}$$

The evaluation of κ from eq 12 or 13 would obviously be simple if we had direct information concerning δ_l, which, however, we have not. In the remainder of this paper it will be shown how the coordination factor, κ, and the vacancy factor, χ, can be calculated, and we shall demonstrate how these two factors, taken together, can account accurately for the change in volume of various solid substances (including water) on melting.

The Vacancy (Hole) Factor, χ, and Evaluation of κ

From the previous discussions on the melting process, we calculated the concentration of extra holes formed from the crossover vibrations of the solid molecules and thereby "lifted off" as shown in eq 2. The total number of holes is given by eq 4. Let us define the vacancy factor, χ, from eq 4 as

$$\chi = \frac{1}{2}(e^{-\theta_m/T'} + e^{-2\theta_m/T'}) \tag{14}$$

which is the mole fraction of vacancies in the liquid system at T_m. This number of holes should occupy a volume of

$$\kappa V_s \chi = V_h = V_l - \kappa V_s \tag{15}$$

from which

$$\kappa = V_l / V_s(1 + \chi) \tag{16}$$

To evaluate χ, we need V_s, T_m, M, $C_{p(m)}$, ΔH_m, and Lindemann's constant L. To evaluate κ, we need V_l and χ. We have already defined θ_m as the characteristic temperature at the melting point, corresponding to the crossover vibrational frequency ν_m. Then

$$\theta_m = h\nu_m / k = E_m / R \tag{17}$$

Substituting Lindemann's expression for ν_m into eq 17 we get

$$\begin{aligned}\theta_m &= L\left(\frac{h}{k}\right)(T_m)^{1/2}(M)^{-1/2}(V_s)^{-1/3} \\ &= L'(T_m)^{1/2}(M)^{-1/2}(V_s)^{-1/3}\end{aligned} \tag{18}$$

where $L' = L(h/k)$ is a new constant. In most cases, $L = 2.8 \times 10^{12}$, so L' should be 1.35×10^2, but for solid noble gases we shall adopt Clusius' modified[18] L', which is 1.63×10^2.

In what follows, we list the values used to calculate θ_m, T', χ, and κ for several substances. The formulas used for calculating these quantities follow: for θ_m, eq 18; for κ, eq 16; for χ, eq 14; for T', eq 3.

The calculated χ values are around 10^{-1}, which is much larger than 10^{-5}, confirming here that our earlier approximation[16] was reasonable. The appropriate data are shown in Table I along with the results of the calculations.

Discussion of the Calculated Data

The noble-gas molecules are spherical. As we go from Ar to Xe, the χ value increases and the θ_m value decreases. The decrease of θ_m means that the shape of the potential well changes, and for a fixed frequency the corresponding vibrational amplitude for Xe is larger than those for Kr and Ar. Since ΔH_m is also larger for Xe than for Kr and Ar, more empty sites are formed in Xe than in the other two. As for N_2, H_2O, and Hg, the difference in χ values is caused by the magnitude of ΔH_m introduced. The extremely low θ_m value for Hg is characteristic of many metals.

The κ values are striking, showing that every substance, theoretically, when changing from solid to liquid, tends toward a more compact packing. To be more exact, they tend to have a closer packed hypothetical liquid quasi-lattice structure. From our previous discussions of κV_s, we see that κ actually reveals how the molecules make use of the "dead space" in the solid which becomes occupiable as quasi-lattice sites in the liquid. In other words, κ indicates the difference in the fraction of volume available for occupation by the fraction of allowed lattice sites in a unit cell in the liquid, compared to that in the solid. Therefore, the number of lattice sites in a unit cell should be inversely proportional to the total volume. Let us define z_l as the number of the nearest-neighbor quasi-lattice sites in the liquid and z_s as the number of nearest-neighbor lattice sites in the solid. Then

$$\kappa = \kappa V_s / V_s = z_s / z_l \tag{19}$$

Since a liquid actually does not have a lattice structure, the proposed quasi-lattice structure is only a convenient theoretical model; consequently, z_l could be larger than 12. For $z_l > z_s$, we have $\kappa < 1$, meaning that a molecule in the liquid will have more nearest-neighbor sites than in the solid, which indicates that the liquid is, inherently, more compact. The calculated κ values, which are less than one for all the substances in Table I, imply that the change in the number of nearest-neighbor sites represents a negative term in the volume change from solid to liquid. On the other hand, χ represents a positive term, and the

Table I. Physical Data Used and Calculated Values of T', θ_m, χ, and κ

	Ar	Kr	Xe	N_2	H_2O	Hg
T_m, K	83.85	116.0	161.3	63.14	273.0	233.3
M	39.95	83.80	131.3	28.01	18.02	200.6
V_s, cm^3	24.98	28.41	36.50	29.31	19.623	14.13
V_l, cm^3	28.03	34.13	42.68	31.95	18.003	14.65
ΔV_m, %	12.2	20.1	16.9	9.00	−8.26	3.67
$C_{p(m)}$, cal/mol·K	7.81	5.05	5.04	11.09	9.03	6.76
ΔH_m, cal/mol	10.71	27.65	56.46	171.0	1436.0	560.0
T', K	85.2	121.5	172.5	78.6	432.0	316.1
θ_m, K	80.65	62.76	54.21	71.99	213.4	65.92
χ	0.269	0.476	0.632	0.280	0.491	0.735
κ	0.884	0.814	0.716	0.852	0.614	0.597

net volume change is due to the combination of these two opposing factors. The reason that a solid tends to become more *compact* upon *melting* is that, in the solid phase, the rigid lattice structure causes a fraction of the solid volume to be "frozen in" as dead space, δ, between the lattice sites. A molecule can only occupy a lattice site or diffuse among lattice sites, but cannot occupy the space between the lattice sites.

According to the mode of packing and the molecular size, δ varies from substance to substance, and can be calculated for solids by the following formula if the index of refraction of the solid is available:

$$\delta_s = V_s - R_m(s) = \left(1 - \frac{n_D^2 - 1}{n_D^2 + 2}\right)_s \frac{M}{d_s} = \left(\frac{3V}{n_D^2 + 2}\right)_s \qquad (20)$$

For ice, the calculated percentage for δ_s is 80.6%. If the refractive index of the solid is not available, we can still calculate δ_s approximately from the refractive index of the liquid or the gas by using the relationship of eq 9. The estimated percentages for δ_s for Ar, N_2, and Hg are 72.9, 85.8, and 64.5%, respectively.

No matter how compactly packed are the molecules, there will always exist a certain amount of dead space. Upon melting, the rigidity of the solid lattice disappears, and the molecules tend to utilize all the space possible, so that the dead space tends toward a minimum.

The notion that κ could become less than one upon melting might previously have been considered reasonable only for those few substances which are known to contract on melting. But the κ values in Table I indicate that even the simplest noble gas solid will, theoretically, contract upon melting, as should H-bonded H_2O, and metallic Hg.

Confirmation of the Validity of the Calculated χ and κ Values

If we can use these calculated values of χ and κ to predict some of the known physical properties, we can verify the validity of this approach. What follows is an attempt at such verification.

The average number of nearest neighbors in several liquids is known by X-ray diffraction. From the nature of χ and κ, we see that these might be used to predict the average number of nearest neighbors for liquids at their melting point, given their number in the solid state. We choose this property to verify the argument because the derivations of χ and κ are not related in any way to the X-ray diffraction data. This choice will, therefore, provide an independent confirmation.

z_l and z_s represent the number of nearest-neighbor "quasi-lattice sites" in the liquid, and actual lattice sites in the solid, and we let x_l and x_s represent the number of nearest *neighbors* in the liquid and in the solid, respectively. These are called the coordination *numbers*, which are therefore the number of nearest neighbor *sites occupied* by molecules in the two phases. X-ray diffraction data will give us information about x but not z.

Table II. z_s and Calculated Values for z_l and x_l Compared with Experimental x_l Values

	Ar	Kr	Xe	N_2	H_2O	Hg
z_s or x_s	12	12	12	12	4	6
z_l	13.6	14.7	16.7	14.1	6.51	10.0
x_l (calcd)	10.7	10.0	10.3	11.0	4.36	5.79
x_l (exptl)	~10.5-10.8	~10.0	~10.2	[a]	~4.4	[a]

[a] Experimental value not available.

As noted previously, the number of empty sites in the solid is of the order of 10^{-5}–10^{-9} mol.[16] To a first approximation, we assume that all the lattice sites are occupied in the solid state, and

$$z_s = x_s \qquad (21)$$

But since $\kappa = z_s/z_l$ (eq 19), it follows that

$$z_l = z_s/\kappa \qquad (22)$$

The total number of molecules in the liquid is the same as that in the solid, but the liquid contains, in addition, χ mol of empty sites. Therefore, the total number of moles of lattice sites in the liquid is $(1 + \chi)$, whereas in the solid it is one. Consequently, the probability of a site being occupied by a molecule in the liquid is $(1 + \chi)^{-1}$; hence

$$x_l = \frac{z_l}{(1 + \chi)} \qquad (23)$$

Substituting eq 21 and 22 into (23) produces

$$x_l = \frac{x_s}{\kappa(1 + \chi)} \qquad (24)$$

The calculated z_l and x_l and experimental x_l values are listed in Table II.

We see from Table II that the calculated x_l compares quite favorably with the experimental value for all substances considered. We should point out that all the experimental x_l values were obtained at temperatures higher than the melting point, and we should perhaps take into consideration the change of x_l with increasing temperature. The agreement with X-ray diffraction data would indicate that our basis for the derivation of χ and κ is correct.

Change of Volume on Melting of a Solid

The percent change of volume on melting, $10^2\Delta V_m$, can be calculated by rearrangement of eq 16 to give

$$\Delta V_m = \kappa V_s(1 + \chi - 1/\kappa) = V_l\left[1 - \frac{1}{\kappa(1 + \chi)}\right] \qquad (25a)$$

and

$$10^2\Delta V/V_s = 10^2\kappa(1 + \chi - 1/\kappa) \qquad (25b)$$

Since the "κ" formula is derived and calculated by using the 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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An Investigation of the Reduction of Aryldiazonium Ions by Hydrazines

William T. Evanochko and Philip B. Shevlin*

Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36830.

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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

$$\begin{tikzcd}
\mathrm{ArN_2^+ + Ar'NHNH_2} \arrow[r, "-\mathrm{H}^+"] & \underset{\mathbf{1}}{\mathrm{ArN{=}NNHNHAr'}} \arrow[dl, "a"'] \arrow[d, "b"] \\
\mathrm{ArNH_2 + Ar'N_3} & \mathrm{ArN_3 + H_2NAr'}
\end{tikzcd} \qquad (1)$$

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

$$\begin{array}{ccccccc}
\mathrm{PhN_2^+BF_4^-} & + & \mathrm{H_2NNHPh} & \xrightarrow{\mathrm{CH_3CN}} & \mathrm{PhH} & + & \mathrm{PhNHNHPh} \\
\mathbf{2a} & & \mathbf{3a} & & 54\% & & 5.8\%
\end{array}$$

$$\begin{array}{cccccc}
+ \mathrm{PhPh} & + & \mathrm{PhN_3} & + & \mathrm{PhNH_2} & (2) \\
1.7\% & & 6.7\% & & 7.7\% &
\end{array}$$

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 ^{1}H 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

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