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Donor Properties of Some Tetraalkoxysilanes toward Iodine

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Complexes of iodine with several $Si(OR)_4$ donors, where R = methyl, ethyl, and *n*-propyl, in *n*-heptane solution have been studied spectrophotometrically over a temperature range of 30°. Thermodynamic properties of the complexes and the spectral characteristics of the complexed iodine visible band are reported. The donor strengths of these tetraalkoxysilanes are rather similar. All are weaker donors toward iodine than diethyl ether.

Introduction

Electron donor properties of alkanes[1] and of carbon compounds containing heteroatoms[2,3] have been studied quite extensively. On the other hand, relatively little has been done on analogous silicon compounds. Traven and West[4] have reported recently the appearance of charge-transfer (CT) bands for permethylpolysilanes as donors and tetracyanoethylene as the acceptor. These spectra apparently are of the contact charge-transfer type.[5] Comparable spectral results on this system have been reported also by Sakurai, Kira, and Uchida.[6]

Some years ago, Shinoda and Hildebrand[7,8] concluded from solubility and spectral studies that octamethyl-*cyclo*-tetrasiloxane is a "violet" or regular solvent for iodine whereas tetraethoxysilane is a "brown" or complexing solvent. The lack of formation of a CT complex in the case of octamethyl-*cyclo*-tetrasiloxane was attributed to the shielding of the oxygen atoms by the methyl groups from the close approach of the iodine.

Tetraalkoxysilanes have been used as solvents to study acid–base reactions. These include aniline derivative donors with picric acid as the acceptor in tetramethoxysilane,[9] tetraethoxysilane,[10] and tetra-*n*-propoxysilane[11] and also *N*,*N*′-diphenylguanidine bases with 2,4-dinitrophenol and some benzoic acid derivatives in tetramethoxysilane[12] and tetraethoxysilane.[13] In the absence of quantitative information on solvent influence[14,15] it is apparent that such studies can give only the *relative* order of base strengths.

Attempts to cleave the Si–OR bond in alkoxysilanes using various reagents[16] have led to the conclusion of prior complex formation. Evolution of heat on mixing $Si(OC_2H_5)_4$ with PBr_3 is attributed to complexation.[17] (In this case, PBr_3 is considered to be the donor and the SiO–R bond is cleaved.) With tin(IV) chloride as the acceptor, a 1:1 complex with tetraalkoxysilanes has been found,[18] as have also a 3:2 complex for the binary mixture of $Si(OC_5H_{11}\text{-}s)_4$–$SnCl_4$ at 20° and a 4:1 complex for the same system[19] in benzene at 5°.

Quantitative information on the donor properties of tetraalkoxysilanes is very limited. From cryoscopic measurements of the system $Si(OC_4H_9)_4$–$SnCl_4$ in benzene, an average equilibrium constant of 26 M^{-1} was obtained for the formation of the 1:1 complex.[20] Also, spectrophotometric studies of $Si(OC_2H_5)_4$–I_2 in carbon tetrachloride[21] led to an association constant at 20° reported between 19 and 55 M^{-1}. This result seems high since, as is stated, d_π–p_π bonding in Si–O should weaken the donor properties of oxygen;[21] yet this constant is appreciably larger than that for the diethyl ether–iodine complex.[22,23]

In this paper we report on the quantitative spectral and thermodynamic characteristics of several tetraalkoxysilane–iodine complexes in *n*-heptane, where the alkoxy group is methoxy, ethoxy, or *n*-propoxy.

Experimental Section

Reagents. Iodine (J. T. Baker) was purified as described previously.[23] *n*-Heptane (Eastman Spectro Grade) was used without further purification.

Tetramethoxysilane (Eastman), tetraethoxysilane (Aldrich Chemical), and tetrapropoxysilane (PCR, Inc.) were purified by keeping them in contact with sodium metal overnight. The liquid was then decanted and distilled under nitrogen gas through a 6-in. Vigreux column packed with glass helices. The distillation was repeated two more times, taking only the middle cut each time. In the case of the *n*-propoxy compound, the distillation was carried out at 25 Torr. The densities of the liquids matched well the literature values for tetraethoxysilane (at 20.0°; found 0.9335 g ml^{-1}, lit.[24] 0.9345 g ml^{-1}) and tetrapropoxysilane (at 20.0°; found 0.9103 g ml^{-1}, lit.[25] 0.9105 g ml^{-1}) but the value was slightly different for the tetramethoxysilane (at 20.0°; found 1.0413 g ml^{-1}, lit.[26] 1.032 g ml^{-1}). Densities of tetraalkoxysilane–*n*-heptane mixtures were determined over the temperature range 10.0–35.0°. These data[27] show there is a difference from volume additivity, although the deviation is not large and is particularly small for the tetrapropoxysilane–*n*-heptane system.

Apparatus. Initial spectral measurements were carried out with a Cary 14 recording spectrophotometer to determine the optimum range of donor and acceptor concentrations to use in the study and also to determine the general features of the spectral bands. The evaluation of the thermodynamic characteristics of the complexes was made from point by point absorbance readings on nine solutions of each system in the donor concentration range ~0.3 to ~2.5 *M* using a Beckman DU spectrophotometer equipped with Beckman thermospacers for temperature regulation. Temperature control was maintained by circulating water with a Haake Model FK constant-temperature circulator. The cell temperature differed slightly from the bath temperature as determined by thermocouple measurement, amounting to ~0.5°/10° difference from room temperature, because of heat exchange through the connecting tubing. Dry air was passed through the cell housing at low temperatures to prevent fogging. All cells used were of 1.000 ± 0.002 cm cell path.

Calculations. The determination of the association constant, *K*, and extinction coefficient, ϵ, was based on a least-squares analysis (using a computer program) of eq 1 where D_0 and A_0 are the initial concentrations of donor and acceptor, Abs is absorbance, *b* is the length of the cell, and ϵ_c and ϵ_{I_2} refer to the complexed and free iodine species, respectively.

$$\frac{D_0 b A_0}{\text{Abs}} = \frac{D_0 + A_0}{\epsilon_c - \epsilon_{I_2}} + \frac{1}{K(\epsilon_c - \epsilon_{I_2})} - \frac{\text{Abs}}{b(\epsilon_c - \epsilon_{I_2})^2} \qquad (1)$$

This equation is applicable to the case where absorption by the cell containing the complex is measured against a reference cell containing the same iodine concentration in *n*-heptane, care being taken to ensure that the matching was fairly exact. The spectra obtained in this way gave a broad maximum at ~464 nm, and the absorbance data at this wavelength were used for the calculation in eq 1.

Actually, for relatively weak complexes, dropping the last term in eq 1 has practically no effect on the *K* and ϵ values.[15,28] The resulting linear equation is then of the Scott type.[29] Plots of the data in this way showed very good linearity.

Results

The spectrum of an *n*-heptane solution 2.5 *M* in tetraethoxysilane and 1.0 × 10^{-3} *M* in iodine in a 1.00-cm cell showed a blue shift of the visible iodine band but failed to show any distinct CT band, at least down to a wavelength of 240 nm. At this relatively high iodine concentration, the contact-charge-transfer band for *n*-heptane–iodine[30] is already

Table I. Tetraalkoxysilane–Iodine Complexes in *n*-Heptane[a]

	$Si(OCH_3)_4$–I_2		$Si(OC_2H_5)_4$–I_2		$Si(OC_3H_7)_4$–I_2	
T, °C	K_c, M^{-1}	$\epsilon_c - \epsilon_{I_2}$,[b] M^{-1} cm^{-1}	K_c, M^{-1}	$\epsilon_c - \epsilon_{I_2}$,[b] M^{-1} cm^{-1}	K_c, M^{-1}	$\epsilon_c - \epsilon_{I_2}$,[b] M^{-1} cm^{-1}
10.50	1.21 ± 0.09	602 ± 16	1.05 ± 0.05	666 ± 13	0.83 ± 0.04	670 ± 14
14.80	1.10 ± 0.07	601 ± 16	0.95 ± 0.06	662 ± 18	0.78 ± 0.04	661 ± 15
19.90	0.98 ± 0.08	602 ± 20	0.85 ± 0.05	663 ± 17	0.69 ± 0.03	661 ± 17
24.75	0.94 ± 0.07	578 ± 18	0.79 ± 0.05	653 ± 20	0.63 ± 0.05	657 ± 25
33.40	0.78 ± 0.10	572 ± 34	0.65 ± 0.04	649 ± 22	0.53 ± 0.03	652 ± 30
38.80	0.73 ± 0.10	560 ± 36	0.60 ± 0.05	641 ± 31	0.50 ± 0.04	637 ± 30

[a] Error limits at 95% confidence level. [b] At λ 464 nm (ϵ_{I_2} 247 M^{-1} cm^{-1}).

Table II. Spectral and Thermodynamic[a] Data for Tetraalkoxysilane–Iodine Complexes in *n*-Heptane[b]

	$Si(OCH_3)_4$–I_2	$Si(OC_2H_5)_4$–I_2	$Si(OC_3H_7)_4$–I_2
λ_{max},[c] nm	477	476	479
ϵ at λ_{max}, M^{-1} cm^{-1}	910	970	990
$\nu_{1/2}$, cm^{-1}	3650	3720	3560
K_{298}, M^{-1}	0.92 ± 0.07	0.78 ± 0.05	0.63 ± 0.05
ΔG°_{298}, kcal mol^{-1}	0.053 ± 0.045	0.151 ± 0.038	0.273 ± 0.043
ΔH°, kcal mol^{-1}	−3.1 ± 0.4	−3.5 ± 0.2	−3.3 ± 0.3
ΔS°, cal mol^{-1} deg^{-1}	−10.7 ± 1.3	−12.1 ± 0.8	−11.8 ± 1.1

[a] Relative to a standard state where the concentrations of donor, acceptor, and complex are 1 M. [b] At 95% confidence level. [c] Blue-shifted iodine band.

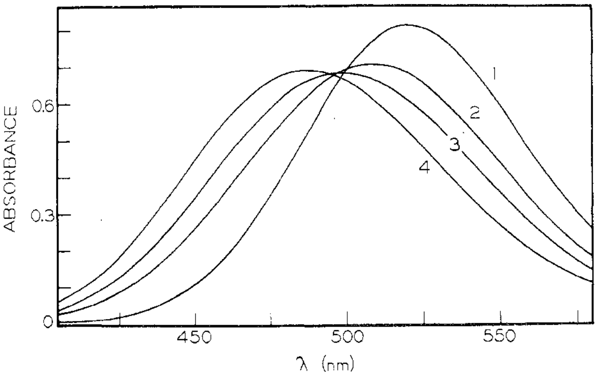

Figure 1. Visible spectra of $Si(OCH_3)_4$–I_2 in *n*-heptane; temperature 23.4°, cell path 1.000 cm; $[I_2] = (8.96 \pm 0.03) \times 10^{-4}$ M with $Si(OCH_3)_4$ concentrations of (1) 0, (2) 0.494 M, (3) 1.033 M, and (4) 2.189 M.

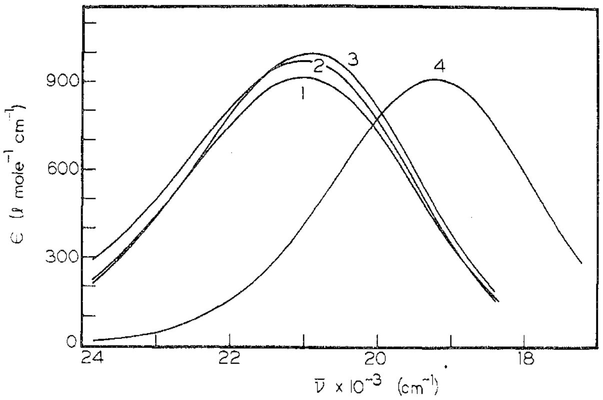

Figure 2. Extinction coefficients in *n*-heptane of the complexed and free visible iodine bands: (1) $Si(OCH_3)_4$–I_2; (2) $Si(OC_2H_5)_4$–I_2; (3) $Si(OC_3H_7)_4$–I_2; (4) free I_2.

at an absorbance above 2 near 240 nm. Therefore, the study was limited to only the visible region.

The effect on the visible iodine spectrum due to the interaction of the tetramethoxysilane with iodine is shown in Figure 1 obtained with the Cary 14 spectrophotometer using pure *n*-heptane in the reference cell. Similar spectra were obtained for the ethoxy and *n*-propoxy compounds.[27] In each case, a blue shift of the iodine band due to complexation is observed. There is no well-defined isosbestic point; rather there is observed a slight shift to lower wavelength with increase in donor concentration. A possible explanation is that this may be due to formation of higher complexes,[31] say 2:1, at the high donor concentration used. However, such formation probably is small because, as mentioned in the Experimental Section, a Scott-type plot based on 1:1 complexation showed good linearity; also analysis of this system by Deich[21] using Job's method indicated 1:1 complexation (although the total concentration of donor plus acceptor was only 0.08 M). Another possibility is a change in the extinction coefficient as a result of the appreciable change in the nature of the medium over this large range of alkoxysilane concentrations[32] (e.g., change in refractive index[33]).

The values of K and ϵ obtained from the spectral data taken with the Beckman DU spectrophotometer are given in Table I. The error limits at the 95% confidence level are relatively small. There is an apparent trend, although not systematic, of a decrease in $\epsilon_c - \epsilon_{I_2}$ with increase in temperature, no doubt due to temperature broadening. From the K values it was possible to calculate the concentrations of both the free and complexed iodine in solution. Subtracting the contribution of the free iodine from the total absorbance gave the spectra of the complexed iodine shown in Figure 2.

A differential method for determining the blue-shifted iodine band directly makes use of maintaining an iodine equilibrium between two tetramethylammonium polyiodide solids,[34,35] i.e., a polyiodide mixture in the reference cell and donor plus polyiodide mixture in the sample cell. This method was tried for tetraethoxysilane (2.18 M) with the solids $(CH_3)_4NI_9$–$(CH_3)_4NI_5$. The spectrum obtained showed the blue-shifted iodine band, but there appeared also two strong peaks at 290 nm and 360 nm which are characteristic of I_3^-. The tail of the 360-nm band overlapped with the blue-shifted iodine band, and this undoubtedly is the cause for the apparent maximum of the complexed iodine band to be observed at 470 nm rather than 476 nm as shown in Figure 2. Formation of I_3^- in alcohol–*n*-heptane mixtures also has been observed when trying this technique.[36] Apparently, I_3^- formation is aided by solvent polarity and small amounts of moisture.[37]

The composite spectral and thermodynamic characteristics of the alkoxysilane–iodine complexes are summarized in Table II.

Discussion

The results in Table II show that the tetraalkoxysilanes are relatively weak donors toward iodine. First, the position of the complexed iodine band shows a smaller blue shift than that generally reported for other oxygen donor compounds,[38] e.g., 470 nm for diethyl ether–iodine.[39] The spectra in Figure 2, with maxima given in Table II, were obtained from data on the most concentrated alkoxysilane solutions, ~2.5 *M*. Actually, there seemed to be a slight shift of λ_{max} to longer wavelengths for solutions of lower donor concentrations, e.g., a shift of ~2 nm when the alkoxysilane concentration was ~0.3 *M*. The value of λ_{max} 476 nm for $Si(OC_2H_5)_4–I_2$ is in good agreement with that of 475 nm reported by Shinoda and Hildebrand[7] for iodine in pure tetraethoxysilane (which is 4.46 *M* at 25°).

The thermodynamic results are consistent with the observed small blue shift. The $\Delta H°$ values are somewhat smaller than that obtained for diethyl ether–iodine in *n*-heptane (-4.2 ± 0.2 kcal mol^{-1}).[1,23] The *K* values for the iodine complexes are similar for diethyl ether ($K_{298} \approx 0.9\ M^{-1}$)[1,23] and the alkoxysilanes. This similarity is due to an entropy effect, which arises from the fact that there are four bonding sites per molecule in the tetraalkoxysilanes compared to only one in diethyl ether. (If, for example, the entropy change in forming the tetraethoxysilane–iodine complex is corrected by the factor $R \ln 4$, then a value for K_{298} of 0.21 M^{-1} is obtained.) Thus the overall results show that these alkoxysilanes are weaker donors than diethyl ether toward iodine.

Further confirmation for the present results can be obtained from analysis of the solubility data of Shinoda and Hildebrand.[7] At 25°, the solubility of iodine in octamethyl-*cyclo*-tetrasiloxane, a "violet" solvent, corresponds to a 0.0367 *M* solution. If it is assumed that the solubility of iodine in tetraethoxysilane, a "brown" solvent, in excess of the above concentration is due to 1:1 complex formation, then a complex concentration of 0.232 *M* is obtained. Since the concentration of pure donor is 4.46 *M*, the calculated association constant at 25° is 1.41 M^{-1}. This value is only a little higher than that reported in Table II. This agreement is quite satisfactory, considering that the pure alkoxysilane is a more polar medium.[40] It must be concluded that the much higher association constant reported by Deich[21] is in error.

A check on $\Delta H°$ also can be made. The paper of Shinoda and Hildebrand[7] contains data for the temperature dependence of the solubility of iodine in octamethyl-*cyclo*-tetrasiloxane at five temperatures over a 20° range and of iodine in tetraethoxysilane at three temperatures over a 13° range.[7] From these data it is possible, as above, to calculate *K* for tetraethoxysilane–iodine at other temperatures. The plot of ln *K* vs. $1/T$ gave a very good line, the slope of which gave the result of -3.0 kcal mol^{-1} for $\Delta H°$. This is of a magnitude comparable to that reported in Table II.

The similarity in the spectroscopic and thermodynamic properties of the iodine complexes with all three tetraalkoxysilanes shows that there are no appreciable steric effects, at least through the *n*-propyl group. Therefore, it seems plausible to explain the solubility data of Shinoda and Hildebrand in terms of the much stronger electron donor ability of the Si–O–C group compared to the Si–O–Si group, as reported by Voronkov and Deich,[41] rather than attribute them to a steric factor.

Arranging the alkoxysilanes studied here in the order of donor strength is difficult. Toward iodine, the *K* value for the donor $Si(OCH_3)_4$ is only slightly larger than that for $Si(OC_2H_5)_4$, being not much outside experimental error. (The values for the $K\epsilon$ products are even closer.) The *K* (and also $K\epsilon$) for $Si(OC_3H_7)_4$ is a little smaller. The $\Delta H°$ and $\Delta S°$ results (Table II) are all within experimental error. They would be even closer if it is recognized that a small difference arises because of the apparent experimental result that there is a somewhat larger temperature dependence of ϵ for $Si(OCH_3)_4–I_2$ than for the two other complexes. If evaluation were to be based on the $K\epsilon$ product (which is equivalent to taking an average value for ϵ over the temperature range), then the following results for $\Delta H°$ and $\Delta S°$ are obtained: -3.6 ± 0.2 kcal mol^{-1} and -12.3 ± 0.7 cal mol^{-1} deg^{-1} for $Si(OCH_3)_4–I_2$, -3.7 ± 0.2 kcal mol^{-1} and -12.9 ± 0.5 cal mol^{-1} deg^{-1} for $Si(OC_2H_5)_4$, and -3.5 ± 0.2 kcal mol^{-1} and -12.7 ± 0.7 cal mol^{-1} deg^{-1} for $Si(OC_3H_7)_4–I_2$.

Small differences in donor properties have been found in other systems, but the trends do not appear systematic. The solubility of HCl in these tetraalkoxysilanes is reported[42] to be in the order $Si(OCH_3)_4 < Si(OC_2H_5)_4 \simeq Si(OC_3H_7)_4$. The equilibrium constant for the aniline–picric acid system also is smallest in $Si(OCH_3)_4$ solvent,[9–11] but in terms of solvent competition this would give the reverse order for the solvent donor strength. Differences in solvent stabilization as a result of interaction at local sites is always a possibility, but these are difficult to predict.

Estimation of the ionization potentials (IP) of donors can be made from the positions of CT bands.[43] Traven and West[4] (using TCNE) found that the IP's of the permethylpolysilanes they studied are in the range ~7.8 to ~8.7 eV. Our qualitative search for a CT band with the tetraethoxysilane–iodine system leads us to suspect it may well be below 230 nm, i.e., below the CT band for ethyl alcohol–iodine.[37] This would put a lower limit of ~10.5 eV[44] on the IP of the tetraalkoxysilanes.

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Registry No. $Si(OCH_3)_4–I_2$, 55800-35-6; $Si(OC_2H_5)_4–I_2$, 43132-01-0; $Si(OC_3H_7)_4–I_2$, 55800-36-7.

Supplementary Material Available. Table III giving density data for alkoxysilane–*n*-heptane mixtures at five temperatures in the range 10.0–35.0°, Tables IV–VI giving data on the concentrations of the solutions and the absorbances at six temperatures for each of the tetraalkoxysilane–iodine systems, and Figures 3 and 4 giving spectral data for the tetraethoxysilane–iodine and tetra-*n*-propoxysilane–iodine systems will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50148L-10-75.

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Synthesis of Diazonium Derivatives of $B_{10}H_{10}^{2-}$ from Arylazo Intermediates

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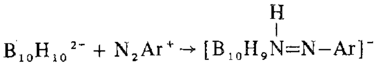
Thermal decomposition of protonated arylazo derivatives of $B_{10}H_{10}^{2-}$ produce diazonium derivatives of $B_{10}H_{10}^{2-}$ plus the arene. A mechanism is suggested which involves electrophilic attack by a proton on the phenyl carbon atom bonded to the azo nitrogen atom. The general utility of this reaction is illustrated by the preparation of a variety of polyhedral B_{10} derivatives.

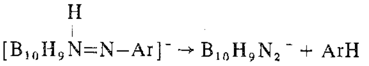
The stable polyhedral borane anion, $B_{10}H_{10}^{2-}$, undergoes a wide variety of reactions in which the hydrogen atoms are replaced by substituent groups.[1] One of the most useful of these substituents is the diazonium function which may itself function as a leaving group in apparent nucleophilic displacement reactions which produce nitrogen. Thus, the N_2^+ function can be readily replaced by a variety of nucleophiles such as CO, NH_3, CH_3CN, C_5H_5N, H_2S, and OH^-.[2] The first reported synthesis of diazonium derivatives of $B_{10}H_{10}^{2-}$ involved the direct reaction of nitrous acid with $B_{10}H_{10}^{2-}$ followed by reduction of an unstable intermediate to the inner diazonium salt.[3] This method gives only $B_{10}H_8(N_2)_2$ and no

$$B_{10}H_{10}^{2-} \xrightarrow[\text{(2) NaBH}_4]{\text{(1) HNO}_2} 1,10\text{-}B_{10}H_8(N_2)_2 \qquad (1)$$

$B_{10}H_9N_2^-$ and has the serious disadvantage that the intermediate may detonate explosively when dry. In a preliminary communication we reported a method of obtaining $B_{10}H_9N_2^-$ and diazonium derivatives of $B_{10}H_9L^-$ from protonated arylazo derivatives[4] and the details of that work are presented here.

Salts of $B_{10}H_{10}^{2-}$, when treated with an aryldiazonium tetrafluoroborate, immediately produce protonated arylazo dyes in nearly quantitative yields.[5] The protonated arylazo species were apically substituted and did not react with a second equivalent of aryldiazonium ion. In addition, the protonated arylazo derivatives were characterized[5] as weak acids in which the nitrogen atom adjacent to the B_{10} polyhedron carried the proton. The protonated arylazo derivatives of $B_{10}H_{10}^{2-}$ and its B-substituted derivatives were found to form the corresponding apical diazonium derivative of the B_{10} polyhedron and the corresponding arene when heated in solution under mild conditions if the aryl group carried electron withdrawing substituents. Due to the general utility of these reactions we believe that they provide the method of choice for the preparation of a wide variety of $B_{10}H_9L^-$ derivatives containing the apical diazonium function.


$$B_{10}H_{10}^{2-} + N_2Ar^+ \rightarrow [B_{10}H_9\overset{\mathrm{H}}{\mathrm{N}}{=}N{-}Ar]^- \qquad (2)$$


$$[B_{10}H_9\overset{\mathrm{H}}{\mathrm{N}}{=}N{-}Ar]^- \rightarrow B_{10}H_9N_2^- + ArH \qquad (3)$$

Results and Discussion

When a solution of $K_2B_{10}H_{10}$ in acetonitrile was treated with 2,4,6-tribromophenyldiazonium tetrafluoroborate at −35° the dark, red, protonated arylazo derivative was formed. If the solution was allowed to come to room temperature and treated with excess sodium propionate, the intensity of the color rapidly decreased and after several hours $(CH_3)_4N[1\text{-}B_{10}H_9N_2]$ was isolated in 52% yield. The neutral B-substituted derivatives $1,10\text{-}N_2B_{10}H_8N(CH_3)_3$, $1,6\text{-}N_2B_{10}H_8N(CH_3)_3$, $1,10\text{-}N_2B_{10}H_8NC_5H_5$, and $1,10\text{-}N_2B_{10}H_8S(CH_3)_2$ were prepared from the correspondingly substituted $B_{10}H_{10}^{2-}$ ions using only slightly more vigorous conditions.

Formation of the diazonium function from the protonated arylazo derivative was found to proceed only very slowly at room temperature in the absence of a weak base. On the other hand, the dianion, $ArN_2B_{10}H_9^{2-}$, was completely unreactive in acetonitrile at the reflux temperature. The most rapid formation of the diazonium function was obtained in the presence of a weak base which apparently had the effect of buffering the arylazo derivative.

These data are consistent with a mechanism for the formation of the diazonium function in which the dianion, $ArN_2B_{10}H_9^{2-}$, is first formed by reaction of the acidic proton with a base, followed by electrophilic attack on the phenyl carbon atom attached to nitrogen by the proton of the conjugate acid of the base.