intermolecular hydrogen bonding, or with *N*-phenethylchloroacetamide (**9**) (mp 67.0–67.5°), a model compound probably incapable of forming such intermolecular hydrogen bonds, were plotted against time. Figure 1 clearly indicates that reaction with $\mathbf{2}_2$ is completed within 1 hr and that $\mathbf{2}_2$ reacts *ca.* nine times as fast as **9** with ethanedithiol at this stage.

From the above results, it seems reasonable to conclude that selective intermolecular association leads to specific synthesis and rate acceleration.

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An Even-Electron, Paramagnetic Silicon Species, $Cl_2Si(bipyridyl)_2$[1,2]

Sir:

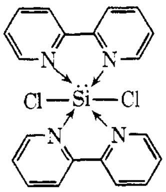
In 1968 Herzog and Krebs[3] reported the synthesis of the intense dark green solid $Cl_2Si(bipy)_2$ (bipy = 2,2′-bipyridyl), slightly soluble in benzene and tetrahydrofuran, by the reaction of $SiCl_4\cdot$bipy with Li_2bipy in tetrahydrofuran.

$$SiCl_4\cdot bipy + Li_2bipy \longrightarrow Cl_2Si(bipy)_2 + 2LiCl$$

The intense green color of the compound is most unusual since all other silicon adducts with nitrogen bases are colorless or nearly so. Recently Kummer, *et al.*,[4] have found that the same compound is formed in a few minutes at room temperature by the reaction of Si_2Cl_6 with bipyridyl in tetrahydrofuran.

$$Si_2Cl_6 + 3bipy \longrightarrow Cl_2Si(bipy)_2 + SiCl_4\cdot bipy$$

The former authors suggested that this compound contained silicon in an oxidation state of +2 and would thus be formulated as a bipyridyl complex of dichlorosilylene, Cl_2Si:, the silicon analog of dichlorocarbene.



In the present study we have found that the solid material exhibits paramagnetic behavior as shown by magnetic susceptibility and epr measurements. The solid as well as the dilute dark green solutions in benzene, toluene, and tetrahydrofuran gave strong, sharp epr signals. The epr signal could be grown controllably in a sealed epr tube by combining Si_2Cl_6, bipyridyl, and tetrahydrofuran at liquid nitrogen temperature, sealing the tube, mixing at −64°, and then measuring the signal at −160°. Only a very weak signal was first observed. On warming to room temperature for approximately 3 min on consecutive occasions, the characteristic green color of $Cl_2Si(bipy)_2$ appeared and the signal (at −160°) grew enormously in intensity. Maximum color and intensity of the signal was reached after about 9 min at room temperature. Identical epr spectra were obtained for samples of $Cl_2Si(bipy)_2$ synthesized either from Si_2Cl_6 and bipyridyl or from $SiCl_4\cdot$bipy and Li_2bipy.

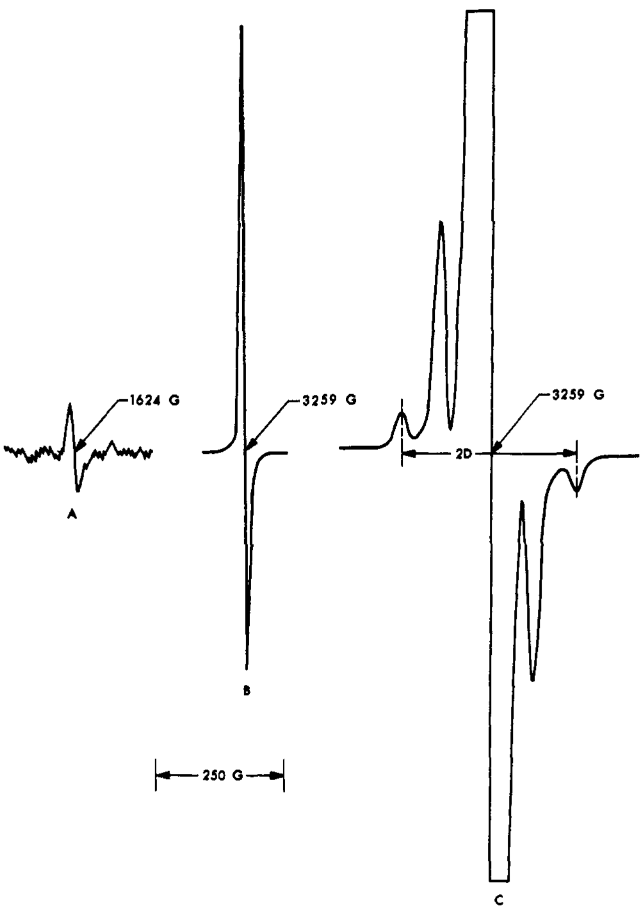


Figure 1. Epr spectrum of a frozen solution of $Cl_2Si(bipy)_2$ in toluene at −160° (ν = 9.137 GHz) recorded at different amplications to show: A, half-field signal; B, center signal; C, triplet signals ($\Delta M = 1$).

The epr spectrum of $Cl_2Si(bipy)_2$ in the form of a solid powder at −160° consisted of a sharp signal at $g = 2.002$ and a weak half-field ($\Delta M_s = 2$) of two different paramagnetic species. The intense sharp signal (width of band envelope, 5 G) at g = 2.002 is believed to be associated with a weakly coupled triplet radical pair. The resonances on either side of the center peak (Figure 1) are clearly due to a triplet species ($g_{x,y}$ = 2.003; g_z = 2.001; D = 172 G). A half-field signal characteristic of a triplet species was also observed (Figure 1). The epr spectra do not show any resolvable nuclear hyperfine splitting. Hyperfine structure is rarely observed in triplets and is not found in the spectra of the related compounds, $Be(bipy)_2$ and $Mg(bipy)_2$, studied by Weissman, *et al.*[5]

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[1] This report is based in part on portions of a thesis to be submitted by P. M. Broudy to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Partial financial support of P. M. B. by the Frankford Arsenal, Philadelphia, Pa., is gratefully acknowledged.

[2] This research was sponsored by AFOSR(SRC)-OAR, USAF Contract No. 70-1836B.

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The molar paramagnetic susceptibility, χ_p ($\chi_p = \chi_M - \chi_d$), of solid $Cl_2Si(bipy)_2$ at 23.3° has a value of 203 ± 10^{-6} cgs unit ($\mu = 0.70$ BM). These data, together with the epr observations, clearly show that the material contains paramagnetic species, but since the moment is considerably less than that expected for a compound containing two unpaired electrons, a diamagnetic species must predominate. The presence of a singlet–triplet spin state equilibrium is suggested by the observation that both the intensity of the epr signal in benzene and toluene solutions and also the magnetic susceptibility of the solid did not follow Curie behavior.

The narrow epr signals with g values close to that of the free electron indicate virtually complete electron transfer of the silicon electrons into the π^* molecular orbitals of the bipyridyl species[6] to form bipyridyl radical anions which are presumably coordinated to the silicon. This conclusion is consistent with the electronic absorption spectrum of $Cl_2Si(bipy)_2$; intense bands which may be assigned to intraligand transitions in coordinated bipyridyl[7,8] and reduced bipyridyl[9,10] are observed at 237, 245, and 282 nm. Also, a very strong band is found at 383 nm with weaker bands at 430 and 473 nm. These are responsible for the intense color of the compound and are probably associated with intraligand transitions in reduced bipyridyl species.[9,10]

The experimental data can be interpreted on the basis of $Cl_2Si(bipy)_2$ being a mixture of two isomers: (i) a hexacoordinate silicon compound, which exists in both singlet and triplet states (this compound may be regarded as being made up of two reduced bipyridyl molecules coordinated to a Cl_2Si group); (ii) a tetracoordinate silicon compound, $[Cl_2Si^{2+}(bipy^-)]^+bipy^-$, which gives rise to the intense, sharp center peak in the epr spectrum[11] (this compound may also be regarded as being made up of two bipyridyl radical anions, only one of which is coordinated to the Cl_2Si group). The weak coupling of the radicals in an ion pair such as this would result from the relatively great separation from each other of the two ($bipy^-$) species. Upon dilution, the intensity of this signal increases relative to that of the triplet signal. This is consistent with an equilibrium of the type[12]

$$Cl_2Si(bipy)_2 \rightleftharpoons [Cl_2Si(bipy)]^+ + bipy^-$$

Our observations show that $Cl_2Si(bipy)_2$ should be formulated as a silicon(IV) compound rather than as dichlorosilylene coordinated to two neutral bipyridyl ligands. We believe that the constitution of $Cl_2Si(bipy)_2$ is very similar to that of $Be(bipy)_2$ and $Mg(bipy)_2$ which have recently been studied by Coates and Green[13] and by Weissman, *et al.*[5] These compounds have characteristic triplet epr spectra with zero-field splittings of 119 and 120 G, respectively, which are of the same order of magnitude as that found in $Cl_2Si(bipy)_2$ (172 G). The paramagnetic susceptibility of $Be(bipy)_2$, although larger than that of $Cl_2Si(bipy)_2$, is significantly less than that expected for two unpaired electrons per molecule.

The conclusions of Coates and Green[13] and of Weissman, *et al.*,[5] concerning the bonding and structure of $M(bipy)_2$ (M = Be, Mg) may be summarized as follows using a valence bond approach. It is suggested that $M(bipy)_2$ exists as a spin equilibrium of species I and II. The diamagnetic, singlet form of $M(bipy)_2$, I, may

$$\underset{\text{I}}{M^{2+}(bipy^0)(bipy^{2-})} \rightleftharpoons \underset{\text{II}}{M^{2+}(bipy^-)(bipy^-)}$$

therefore be formally depicted as containing both a neutral bipyridyl molecule and also a bipyridyl dianion coordinated to an M^{2+} ion. The paramagnetic triplet form, II, consists of two bipyridyl radical anions coordinated to M^{2+}.

We believe the singlet and triplet forms of $Cl_2Si(bipy)_2$ can be explained by an analogous valence bond argument, namely, that the compound exists as a spin equilibrium of species III and IV, the diamagnetic,

$$\underbrace{Cl_2Si^{2+}(bipy^{2-})(bipy^0) \longleftrightarrow Cl_2Si^{2+}(bipy^0)(bipy^{2-})}_{\text{III}} \rightleftharpoons \underset{\text{IV}}{Cl_2Si^{2+}(bipy^-)(bipy^-)}$$

singlet form being the resonance forms of species III and the paramagnetic triplet form being species IV. An average charge of −1 is present on each of the bipyridyls in both species III and IV; the bipyridyls within each species are thus equivalent.

As a means of gaining a more detailed view of the bonding involved in these species, extended Hückel molecular orbital calculations were applied to silicon(bipy) and silicon(diim) (diim = HN=CHCH=NH) model compounds. Ethylenediimine is a structural fragment of 2,2′-bipyridyl with analogous nitrogen donor atoms and low-lying π^* acceptor levels. EHT results indicate that bipyridyl functions exclusively as a donor in $SiCl_4 \cdot bipy$ but additionally functions as a two-electron acceptor in the hypothetical $SiCl_2 \cdot bipy$. The Cl_2Si: fragment is effectively oxidized by bipyridyl to form Cl_2Si^{2+} and $bipy^{2-}$. Oxidation of Cl_2Si: occurs because its highest occupied σ molecular orbital interacts strongly with the bipyridyl σ orbitals thus elevating it well above the lowest empty bipyridyl π^* orbital. The electrons in this highest occupied σ orbital may then be regarded as being transferred to the lower energy orbital in the complex, which is essentially the bipyridyl π^* orbital. Computing size limitations prohibited EHT molecular orbital studies for $Cl_2Si(bipy)_2$ and $Si(bipy)_3$, but calculations were carried out on the model compounds $Cl_2Si(diim)_2$ and $Si(diim)_3$.[14]

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(11) Adducts such as $SiI_4 \cdot 4py$, $SiCl_4 \cdot 4(CH_3)_3PO$, and $SiBr_4 \cdot 4(C_6H_5)_3PO$ have been formulated as $[cis\text{-}I_2Sipy_4]^{2+}2I^-$, $[cis\text{-}Cl_2Si(OP(CH_3)_3)_4]^{2+}2Cl^-$, and $Si[OP(C_6H_5)_3]_4{}^{4+}4Br^-$, respectively [see I. R. Beattie and M. Webster, *J. Chem. Soc.*, 3672 (1965)].

(12) It should be noted that silicon adducts can exist in an equilibrium system in which silicon shows more than one different coordination number, depending on whether one or two ligands are coordinated to the silicon. The system $F_4Si \cdot 2N(CH_3)_3 \rightleftharpoons N(CH_3)_3 + F_4Si \cdot N(CH_3)_3 \rightleftharpoons N(CH_3)_3 + SiF_4$, for example, has been well studied [C. J. Wilkins and D. K. Grant, *ibid.*, 927 (1953)].

(13) G. E. Coates and S. I. E. Green, *ibid.*, 3341 (1962).

(14) Analogous calculations on the model system $Si(diim)_3$, which is representative of $Si(bipy)_3$, show that it has three nearly degenerate π molecular orbitals, derived principally from the diimmine π^* orbitals which accept a total of four electrons from silicon. This is consistent with the observed magnetic properties of $Si(bipy)_3$ reported by Wulf and Herzog [E. Wulf and S. Herzog, *Z.Anorg. Allg. Chem.*, 387, 81 (1972)].

In each case the ligand is found to oxidize the silicon to Si(IV). In *cis*- or *trans*-$Cl_2Si(diim)_2$ there are two closely spaced nearly degenerate ligand π^* orbitals which accept a total of two electrons from Cl_2Si:. The singlet–triplet spin equilibrium in $Cl_2Si(bipy)_2$ must therefore result from this nearly degenerate pair of π^* levels.

From the preceding discussion it follows that the Cl_2Si^{2+} group in $Cl_2Si(bipy)_2$ may be regarded as a positive ion in the same sense that the beryllium and magnesium in $Be(bipy)_2$ and $Mg(bipy)_2$, respectively, are regarded as positive ions. The magnitude of the +2 charge on the silicon will, of course, be somewhat reduced by coordination to the nitrogen atoms, as shown in the molecular orbital calculations. Since the source of the electrons on the bipyridyl dianion or radical anion is the silicon, $[Cl_2Si^{2+}(bipy^-)]^+$ is therefore a four-coordinate nonclassical siliconium ion and species III and IV may be regarded as containing six-coordinate nonclassical siliconium ions.[15] These species are believed to be the first clearly defined examples of stable compounds containing siliconium ions.

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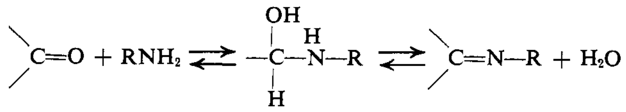
Secondary Deuterium Isotope Effects for Carbonyl Addition Reactions[1]

Sir:

Measurement of kinetic secondary deuterium isotope effects for the addition of amines to benzaldehydes reveals that the extent of progress toward tetrahedral geometry in the transition state is a sensitive function of the structure of substrate, nucleophile, and catalyst. Moreover, in certain cases, proton transfer reactions involving the tetrahedral amine–aldehyde adduct may contribute significantly to both the rate of formation of this adduct and to the rate of its decomposition to imine product.

The addition of simple amines to carbonyl compounds proceeds with rate-determining addition of nucleophile under mildly acidic conditions and with rate-determining dehydration of the tetrahedral intermediate under neutral and basic conditions[2,3]



$$>C{=}O + RNH_2 \rightleftharpoons -\overset{OH}{\underset{H}{C}}-\overset{H}{N}-R \rightleftharpoons\ >C{=}N-R + H_2O$$

In an effort to define the structure of the transition state for these reactions more precisely, measurements of the α-deuterium isotope effects on both rates and equilibria for the addition of semicarbazide and phenylhydrazine to a series of substituted benzaldehydes have been made.

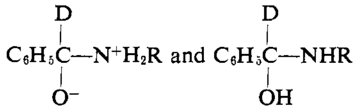
Substituted benzaldehydes-*1-d* were synthesized as previously described.[4,5] Equilibrium constants for addition of hydroxylamine and cyanide to these aldehydes, to yield the corresponding tetrahedral adducts, were measured spectrophotometrically.[6,7] Rate constants for the attack of amines on a series of benzaldehydes and benzaldehydes-*1-d* were also measured spectrophotometrically.[4]

The experimentally determined α-deuterium isotope effects on equilibrium constants for addition of hydrogen cyanide and hydroxylamine to, respectively, *p*-methoxybenzaldehyde and benzaldehyde are collected in Table I. The determined values are in the direction expected by analogy with carbonium ion solvolyses $(>CD{-}OX \rightarrow\ >C^+{-}D + {}^-OX;\ k_H/k_D = 1.23)$[8] but are significantly larger, probably because the stretching force constant associated with the aldehyde C–H bond is low compared to other C(sp^2)–H bonds. The observation that the isotope effect for the addition of the nitrogen nucleophile is greater than that for the carbon one accords with expectations.[8] The value for the addition of hydroxylamine to benzaldehyde serves to provide the basis for interpretation of the kinetic isotope effects described below in terms of the degree of carbon–nitrogen bond formation in the transition state: the isotope effect must increase from unity to 1.36 ± 0.02 as carbon–nitrogen bond formation becomes increasingly complete. This is, of course, based on the reasonable assumption that there would be little or no difference in isotopic fractionation factors between

Table I. α-Deuterium Isotope Effects on the Equilibrium Constants for Addition of Hydrogen Cyanide and Hydroxylamine to Benzaldehydes in Aqueous Solution at 25.00°

Substrate	Nucleophile	K_{eq}^D/K_{eq}^H
p-Methoxybenzaldehyde	Hydrogen cyanide	1.276 ± 0.002^a
Benzaldehyde	Hydroxylamine	1.360 ± 0.020^b

[a] Standard deviation of the mean of three determinations. [b] Standard deviation of the mean of seven determinations.



$$C_6H_5\overset{D}{\underset{O^-}{C}}-N^+H_2R \text{ and } C_6H_5\overset{D}{\underset{OH}{C}}-NHR$$

In Table II, kinetic α-deuterium isotope effects for the water- and acid-catalyzed attack of semicarbazide and phenylhydrazine on three substituted benzaldehydes are collected. Choice of conditions for measurement of these isotope effects was dictated by results of previous studies of the kinetics of these reactions.[9,10]

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[1] Supported by a grant from the National Science Foundation, by Career Development Award No. K3 GM 10248-05, by the Conselho Nacional de Pesquisas, and by the Fundacão de Amparo a Pesquisa de Estado de São Paulo.

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