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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P. M. Broudy, A. D. Berry
B. B. Wayland, A. G. MacDiarmid*

*Department of Chemistry and Laboratory
for Research on the Structure of Matter
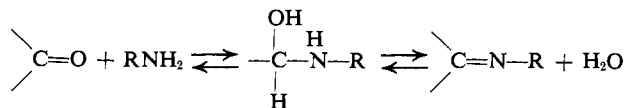University of Pennsylvania
Philadelphia, Pennsylvania 19104*

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]

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

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

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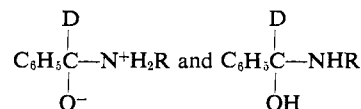
Table I. α-Deuterium Isotope Effects on the Equilibrium Constants for Addition of Hydrogen Cyanide and Hydroxylamine to Benzaldehydes in Aqueous Solution at 25.00°

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.

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

$$\underset{\overset{|}{O^-}}{\overset{\overset{D}{|}}{C_6H_5C}}-N^+H_2R \text{ and } \underset{\overset{|}{OH}}{\overset{\overset{D}{|}}{C_6H_5C}}-NHR$$

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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Table II. Kinetic α-Deuterium Isotope Effects for the Addition of Semicarbazide and Phenylhydrazine to Substituted Benzaldehydes in Aqueous Solution at 25.00° [a]

Nucleophilic reagent	Catalyst	Substrate		
		p-Methoxy	m-Bromo	p-Nitro
Semicarbazide	Hydrated proton[b]	1.216 ± 0.006	1.218 ± 0.004	1.154 ± 0.013
	Water[c]	1.310 ± 0.004	1.288 ± 0.005	1.293 ± 0.009
Phenylhydrazine	Hydrated proton	1.208 ± 0.010		1.126 ± 0.007
	Water	1.276 ± 0.011		1.163 ± 0.006

[a] Errors are given as the standard deviation of the mean of three determinations. [b] Isotope effects for the proton-catalyzed reaction were measured near pH 2. Under these conditions, neither the water reaction nor the rate of carbinolamine dehydration contributes significantly to the overall reaction rate. [c] It is impossible to choose values of pH for the measurement of isotope effects for the water reaction at which other reactions do not make significant contributions to the overall rate. Since the measured isotope effects for the proton-catalyzed attack reaction and the proton-catalyzed dehydration of the carbinolamine are both smaller than the effects measured for the water reaction, the recorded values are minima.

It proved impossible to choose values of pH at which the water-catalyzed attack reaction could be measured independently; generally both the acid-catalyzed attack of the nucleophile and the acid-catalyzed dehydration of the carbinolamine contributed significantly to the observed rate constants even at the optimal values of pH. Consequently, the indicated isotope effects for the water-catalyzed reactions are *minimum* values.

Employing the secondary deuterium isotope effects as indicators of the degree of progress toward tetrahedral geometry (*i.e.*, the extent of carbon–nitrogen bond formation), one may draw the following conclusions. First, the extent of progress along the reaction coordinate at the transition state decreases with (i) increasing substrate reactivity, (ii) increasing reactivity of the nucleophilic reagent, and (iii) increasing acid strength of the catalyst. These observations are all consistent with theoretical expectations[11,12] and with conclusions drawn earlier on the basis of less direct lines of evidence.[2,3,9,10] Second, in the case of the water-catalyzed reactions, it is possible that proton transfer may contribute significantly to the overall rate of carbinolamine formation. This is suggested by the fact that the kinetic isotope effects are nearly as large as the equilibrium ones, indicating that carbon–nitrogen bond formation is nearly complete in the transition state (Tables I and II). This conclusion is, of course, consistent with the observation of general acid catalysis for the attack of nitrogen nucleophiles on carbonyl carbon.[2,3] Third, the smaller kinetic isotope effects for the proton-catalyzed reaction indicate that this is not a diffusion-controlled reaction of the proton with an addition intermediate.

Finally, the kinetic α-deuterium isotope effect for semicarbazone formation in the region of rate-determining acid-catalyzed carbinolamine dehydration has been determined: for m-bromobenzaldehyde k_D/k_H is 1.271 ± 0.009 and for p-methoxybenzaldehyde the corresponding quantity is 1.287 ± 0.015. These values, too, are near the maximum expected indicating that the transition state for carbinolamine dehydration has a nearly tetrahedral geometry.[13] These results accord

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(13) The minimum isotope effect possible, in the region of rate-determining dehydration, that corresponding to a transition state having trigonal geometry (*i.e.*, the semicarbazone itself), must be equal to the isotope effect on the equilibrium constant for the overall reaction. Although this value is not known, it can be approximated from the measured value, *vide supra*, for carbinolamine formation, that k_D/k_H = 1.36, and the maximum kinetic isotope effect observed for the attack of solvent species on Schiff bases is k_D/k_H = 1.22.[14] The calculated value, $(k_D/k_H)_{overall}$ = 1.11.

with earlier findings of large secondary deuterium isotope effects for attack of water and hydroxide ions on protonated Schiff bases.[14] Consequently, it appears possible that, for some cases at least, proton transfer reactions involving interconversion of the various forms of the carbinolamine intermediates partially determine the reaction rate under neutral and basic conditions.

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Luciano do Amaral
*Instituto de Química, Universidade de São Paulo
São Paulo, Brazil*

H. G. Bull, E. H. Cordes*
*Department of Chemistry, Indiana University
Bloomington, Indiana 47401*
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Influence of Ion Pairing on Intramolecular Electron-Transfer Rates in the Anion Radical of 1,2-Di(9-carbazyl)ethane

Sir:

Over the past several years there have been a number of investigations into the modification of the magnetic properties of anion radicals by ionic association.[1,2] Both the structure and the dynamic behavior of ion pairs have been elucidated using magnetic resonance techniques, *e.g.*, splitting due to the cation,[3] line broadening,[4] selective line width effects,[5] and minor changes in proton hyperfine coupling constants and g values.[6] Observation of these various phenomena can be taken as proof of the existence of ion pairing but the converse is not necessarily true. In this communication we report the esr spectra of the anion radicals of N-ethylcarbazole (1) and 1,2-di(9-carbazyl)ethane (2) in tetrahydrofuran (THF) and 1,2-dimethoxyethane

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