

Theoretical Studies on Gas Phase Reaction of Alkoxide-Exchange at Silicon and Carbon Centers[†]

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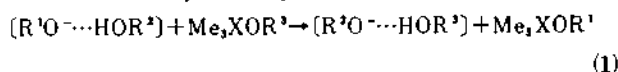
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MNDO and ab initio calculations for gas phase reactions of alkoxide-exchange at silicon and carbon centers have been performed. Results show that MNDO values of ΔE 's of these reactions closely parallel those of the STO-3G method. The alkoxide-exchange at silicon is shown to be facile due to the formation of stable five-coordinate intermediate while the reaction at carbon is predicted to proceed with high barrier; the difference in this substitution behavior between carbon and silicon is shown to be due to an easy valence shell expansion of silicon in accommodating an extra bond in the formation of stable five-coordinate intermediates.

Introduction

Recently ion cyclotron resonance (ICR) spectroscopy has provided a means of studying an interesting class of gas phase reaction involving a cluster anion of the form $[R^1O^-\cdots HOR^2]$, where R^1 and R^2 are alkyl groups.¹ This alkanol-alkoxide negative ion is produced by the Riveros reaction² $R^1O^- + HCO_2R^2 \rightarrow [R^1O^-\cdots HOR^2] + CO$ in ICR experiments. The species $[MeO^-\cdots HOMe]$ is unsymmetrical in the ground state and the barrier for the interconversion $[MeO^-\cdots HOMe] \rightarrow [MeOH^-\cdots OMe]$ is computed to be of the order of 0.5 kcal/mol.^{1(c),3}

Two aspects of the 'alkoxide exchange' reaction (1) have been established by ICR experiments:¹



where $X = Si$ or C and $R^1 < R^2$.

(i) The reaction proceeds by the four-center mechanism for both $X = Si$ and C , the smaller alkoxide R^1O^- reacting predominantly at X and the larger alkanol R^2OH becoming part of the new alkanol-alkoxide ion.

(ii) The reaction is much less pronounced for carbon ethers, *i.e.*, for $X = C$, than that observed for the corresponding silanes, *i.e.*, $X = Si$. On the other hand, theoretical calculations have shown that silicon can form stable five-coordinate adducts even with bulky donor groups.^{1(a),4} This is in contrast with carbon, which is unable to form five-coordinate adducts even with the smallest donor atoms.^{1(a)} Thus the five-coordinate species formed during an S_N2 process like reaction (1) is a stable intermediate for silicon, whereas it is a transition state(TS) for carbon; thus the S_N2 mechanism on silicon never resembles that of carbon.

In this report, we examine MO theoretically the mechanistic pathways of the reaction(1) using ab initio⁵ and MNDO methods⁶ in order to gain further insights into the mechanistic

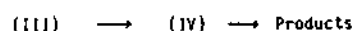
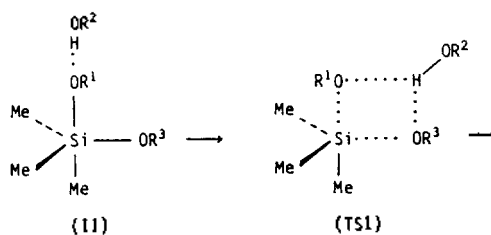
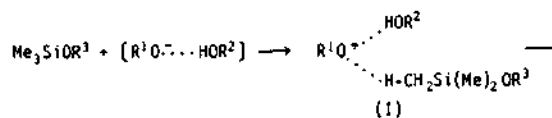
details involved in the reaction(1).

Calculation

Reaction paths were searched using a simplified model (a), $[R^1O^-\cdots HOR^2] + CH_3XH_2OR^3 \rightarrow$ where $R^1 = R^2 = R^3 = H$. In order to study size effect of R^1 and R^2 , we then proceeded with two other models: (b) $R^1 = CH_3$, $R^2 = R^3 = H$, (c) $R^1 = R^2 = H$, $R^3 = CH_3$. Calculations were carried out with MNDO/H^{6a} and STO-3G methods.⁵ All the equilibrium points and TS were located by analytical energy gradient computations,⁷ and the TS's were characterized by confirming that the Hessian matrix had only one negative eigenvalue.⁸

Results and Discussion

(a) The reaction of $CH_3XH_2(OH)$ with $[HO^-\cdots HOH]$. Based on the results of ICR experiments, Hayes *et al.* have suggested the following mechanistic pathways for the reaction(1).^{1(c)}



where intermediates (III) and (IV) are the alkoxide exchange

[†] Determination of Reactivity by MO Theory (Part 41)

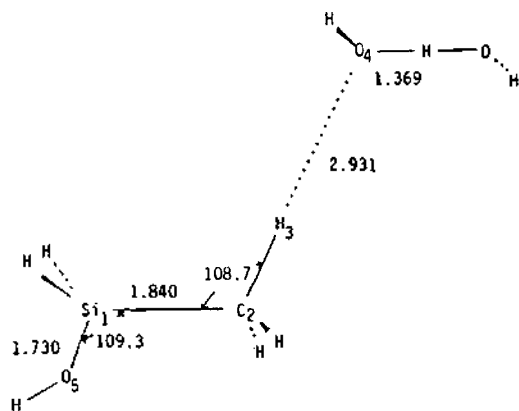
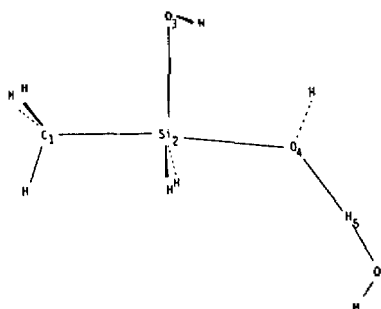


Figure 1. MNDO optimized structure and geometries of intermediate (I). Bond lengths and bond angles are in angstroms and degrees, respectively.

Table 1. Optimized Structure and Geometries of Stable Intermediate(II)



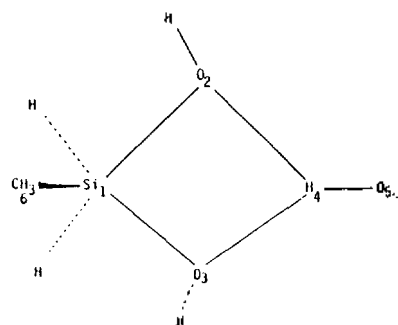
Variable	MNDO	STO-3G
d12	1.942	1.964
d23	1.769	1.716
d24	1.825	1.799
d45	1.515	1.447
a123	94.95	94.27
a324	91.63	86.04
E	-48.5835	-549.5788

*Bond lengths(d) in angstroms; bond angles(a) in degrees; energies(E) in atomic units.

ed($\text{OR}^1=\text{OR}^2$) analogues of the intermediates (II) and (I), respectively. In the model (a), all alkyl groups are equal, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$, so that obviously (I) = (IV) and (II) = (III). We have obtained optimized structures corresponding to intermediates (I), (II), and TS1. The results are given in Figure 1 and Tables 1 and 2.

A cluster anion $[\text{HO}^-\cdots\text{HOH}]$ placed in the vicinity of the methyl group of $\text{CH}_3\text{SiH}_2(\text{OH})$ relaxes to the H-bonded adduct of the type (I). Although a barrier of ~ 8 kcal/mol has been shown to exist before the stable five-coordinate intermediate of the type (II) is formed from (I),¹⁸ we have not elaborated further on this barrier. The adduct of type (II) appears to be a true intermediate having the formation energy of -55 kcal/mol by STO-3G calculations. This value is comparable to the corresponding formation energy for the five-coordinate adduct of OH^- with MeSiH_3 .¹⁸

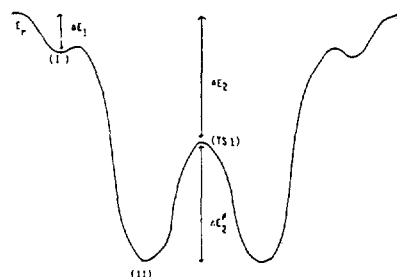
Table 2. Optimized Structure and Geometries of Transition State(TS1)*



Variable	MNDO	STO-3G
d12	1.787	1.739
d13	1.787	1.748
d24	1.844	1.816
d34	1.844	1.817
d16	1.868	1.908
a124	99.20	102.87
a213	82.07	79.17
a243	79.07	75.41
E	-48.5499	-549.5721

*Bond lengths(d) in angstroms; bond angles(a) in degrees; energies(E) in atomic units.

Table 3. Energy Profile and Relative Energies (in kcal/mol) for the Reaction of $[\text{HO}^-\cdots\text{HOH}] + \text{CH}_3\text{SiH}_2\text{OH}^-$



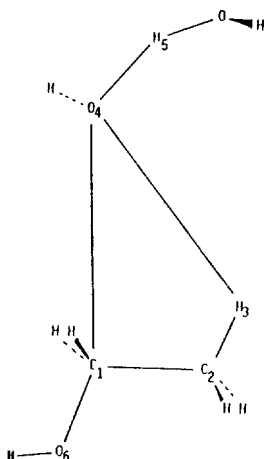
Energies	MNDO	STO-3G
ΔE_1	2.32	
ΔE_2	26.80	37.88
ΔE_1^\ddagger	14.36	16.73
$\Delta E_2 + \Delta E_1^\ddagger$	41.16	54.61
$E_A (= E_p)$	-48.5179	-549.7117

*Total energy(E_A) in atomic units.

The alkoxide exchange barrier, *i.e.*, activation energy for TS1, is a modest one for a gas phase reaction, and the barrier is well below the reactants level so that the exchange should proceed readily. Energy profile for the reaction is presented in Table 3, which provides a strong theoretical support for the suggested mechanistic pathway of Hayes *et al.*¹⁸ based on ICR experiments. It is also notable that the results of MNDO calculations closely parallel those of the STO-3G potential energy profile.

The reaction of a cluster anion $[\text{HO}^-\cdots\text{HOH}]$ with carbon

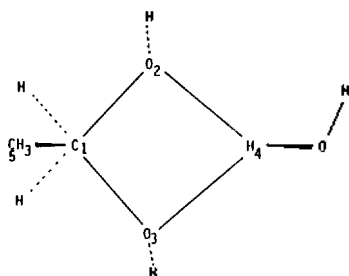
Table 4. Optimized Structure and Geometries of Intermediate(V)*



Variable	MNDO	STO-3G
d12	1.540	1.545
d14	3.760	3.785
d16	1.408	1.442
d34	3.411	3.405
d45	1.369	1.219
a123	109.74	109.24
a412	85.15	91.41
a234	146.33	124.88
E	-49.6764	-301.2791

*Bond lengths(d) in angstroms; bond angles(a) in degrees; energies(E) in atomic units.

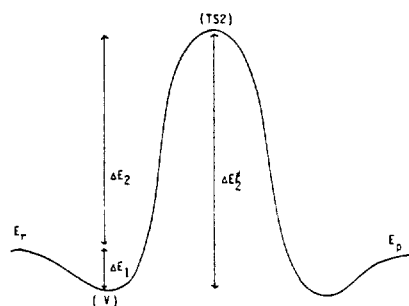
Table 5. Optimized Structure and Geometries of Transition State(TS2)*



Variable	MNDO	STO-3G
d12	1.500	1.666
d13	1.500	1.661
d24	1.776	1.779
d34	1.776	1.779
d15	1.563	1.574
a124	98.53	99.45
a213	88.98	83.61
a243	72.59	77.04
E	-49.5394	-301.1417

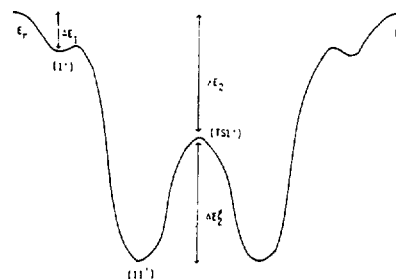
*Bond lengths(d) in angstroms; bond angles(a) in degrees; energies(E) in atomic units.

substrate, $\text{CH}_3\text{CH}_2\text{OH}$, differs markedly from that of the corresponding silicon substrate; there is neither a discrete H-

Table 6. Energy Profile and Relative Energies (in kcal/mol) for the Reaction of $[\text{HO}\cdots\text{HOH}]^-\text{CH}_3\text{CH}_2\text{OH}^-$ 

Energies	MNDO	STO-3G
ΔE_1	2.72	2.05
ΔE_2	83.26	84.18
ΔE_2^\ddagger	85.98	86.23
$E_r (= E_p)$	-49.6721	-301.2759

*Total energy(E_r) in atomic units.

Table 7. Energy Profile and Relative Energies (in kcal/mol) for the Reaction of $[\text{HO}\cdots\text{CH}_3\text{OH}]$ and $[\text{CH}_3\text{O}\cdots\text{HOH}]$ with $\text{CH}_3\text{SiH}_2\text{OH}^-$ 

Energies	$[\text{HO}\cdots\text{CH}_3\text{OH}]$	$[\text{CH}_3\text{O}\cdots\text{HOH}]$
ΔE_1	4.03	1.99
ΔE_2	18.39	9.79
ΔE_2^\ddagger	17.43	10.21
$\Delta E_2 + \Delta E_2^\ddagger$	35.82	20.00
ΔE	0.0	20.94
$(E_r - E_p)$		
E_r	-54.2688	-54.2919

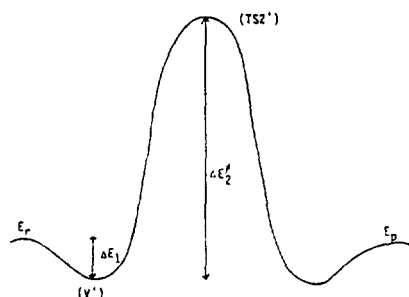
*Total energy(E_r) in atomic units.

bonded adduct of the type (I) nor a five-coordinate adduct corresponding to (II), but there is only one adduct, (V), which resembles a structure in between. Optimized geometries of the adduct (V) are given in Table 4. The exchange barrier in this case is very high and about 5 times of that for the silicon analogue. This constitute a theoretical verification of the ICR results that the alkoxide exchange at carbon is much less reactive than that at silicon center.^{1c} The optimized four-center TS (TS2) is given in Table 5, and the energy profile for the reaction of carbon center is presented in Table 6.

Here again the close agreements between MNDO and STO-3G values of various energy changes are striking.

It is interesting to note that while the alkoxide exchange reaction at silicon center proceeds by a double-well potential energy surface similar to that for the gas phase $\text{S}_{\text{N}}2$ reaction

Table 8. Energy Profile and Relative Energies (in kcal/mol) for the Reactions of $[\text{HO}^{\ominus}\cdots\text{CH}_3\text{OH}]$ and $[\text{CH}_3\text{O}^{\ominus}\cdots\text{HOH}]$ with $\text{CH}_3\text{CH}_2\text{OH}^{\oplus}$



Energies	$[\text{HO}^{\ominus}\cdots\text{CH}_3\text{OH}]$	$[\text{CH}_3\text{O}^{\ominus}\cdots\text{HOH}]$
ΔE	2.54	2.56
$\Delta E_{\ddagger}^{\ominus}$	96.66	109.28
ΔE ($E_p - E_r$)	0.0	27.34
E_r	-55.4230	-55.4460

*Total energy(E_r) in atomic units.

of alkyl halide,⁹ the exchange process at carbon proceeds with a potential energy profile very similar to that for the one step solution phase S_N2 reaction at a saturated carbon center.¹⁰ This suggests the possibility that the solution phase S_N2 reaction at silicon center may also proceed by a double well potential surface involving a stable five-coordinate intermediate of the type (II).

(b) The reaction of $\text{CH}_3\text{XH}_2(\text{OH})$ with $[\text{CH}_3\text{O}^{\ominus}\cdots\text{HOH}]$, and (c) with $[\text{HO}^{\ominus}\cdots\text{HOCH}_3]$. In order to assess the size effect of alkyl groups, R^1 and R^2 in equation (1), on the barrier height, we have computed potential energy profiles for the two cases by MNDO method: (b) $R^1 = \text{CH}_3$, $R^2 = \text{H}$, and (c) $R^1 = \text{H}$ and $R^2 = \text{CH}_3$. The results are summarized in Tables 7 and 8 for $X = \text{Si}$ and C , respectively. Reference to these Tables reveals that the alkoxide exchange at silicon is very little influenced by the size of the alkyl groups in the cluster anion, while an increase in the size of alkyl group causes a substantial elevation of barrier height in the alkoxide exchange at carbon center; barrier height is raised in both cases of (b) and (c) but the elevation is much greater in the case (b), where the group reacting at carbon is the larger. This indicates that for silicon center the effect of size of cluster anion is minimal, whereas for carbon center the effect of alkyl group size, in particular that in alkoxide group, is rather great. We therefore made an energy decomposition analysis of the activation barrier, $\Delta E^{\ddagger} = \Delta(2\Sigma\epsilon_i) - \Delta V_{ee} + \Delta V_{nn}$ where Δ represents the change from intermediate II(V) to TS1(TS2), as shown in Table 9.

This shows that in all cases, irrespective of whether $X = \text{Si}$ or C , the barrier height is determined mainly by the one-electron term, $\Delta(2\Sigma\epsilon_i)$. Although repulsion between atomic cores, ΔV_{nn} , appear to be unfavorable for the large alkyl group in the cluster anion, the effect is more than compensated for by the electronic repulsion term ΔV_{ee} ; the value of $\Delta(V_{nn} - V_{ee})$ is negative in all cases indicating that the steric term⁽¹¹⁾ is actually favorable. Thus for $X = \text{Si}$ the elevation of orbital levels in the four-center TS formation is relatively small, but for $X = \text{C}$ it becomes substantial. The difference between carbon and silicon is therefore due to the increase

Table 9. Energy Components (in eV) of the Activation Barrier($\Delta E_{\ddagger}^{\ominus}$) for the Reactions of $[\text{HO}^{\ominus}\cdots\text{CH}_3\text{OH}]$ and $[\text{CH}_3\text{O}^{\ominus}\cdots\text{HOH}]$ with $\text{CH}_3\text{XH}_2\text{OH}$

Components	$X = \text{Si}$		$X = \text{C}$	
	$R^1 > R^2$	$R^1 < R^2$	$R^1 > R^2$	$R^1 < R^2$
$\Delta(2\Sigma\epsilon_i)$	6.06	10.10	30.86	21.56
ΔV_{nn}	124.94	193.40	728.12	710.32
ΔV_{ee}	130.55	202.74	754.24	727.69
$\Delta(V_{nn} - V_{ee})$	-5.61	-9.34	-26.12	-17.37
$\Delta E_{\ddagger}^{\ominus}$	0.44	0.76	4.74	4.19

in atomic size from C to Si having an effect on bond formation and, in particular, on favoring a greater number of bond formed in the four-center TS. Valence shell expansion in order to accommodate an extra bond formation is relatively easy for Si since the silicon has relatively low lying empty d orbitals, whereas it is a difficult and costly process for carbon atom since the carbon has to utilize high lying d orbitals for the formation of five-coordinate species like the four-center TS2.

We therefore conclude that the difference between nucleophilic substitution behaviors of carbon and silicon is due to the low lying atomic d orbitals available in silicon which can easily accommodate an increase in the coordination number, and not due to steric effects of bulky incoming nucleophiles.

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Synthesis of (E,E)-2,4-Dienols from (E)- β -Chloro- γ -hydroxy-vinylmercurials and Olefins by Palladium(II) Salt

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Reaction of (E)- β -chloro- γ -hydroxyvinylmercurials, prepared by mercuriation of propargyl alcohol and 2-methyl-3-butyn-2-ol, with olefins in the presence of a catalytic amount of Li_2PdCl_4 and 2 equiv of cupric chloride in methanol at 50°C gave the corresponding (E,E)-2,4-dienols in moderate yields. However, addition of 1 equiv of inorganic bases such as magnesium oxide to the reaction mixture brings a rapid and clean vinylation and gave high yields of the dienols at room temperature. In the case of hindered (E)-2-chloro-3-chloromercuri-2-buten-1,4-diol prepared from 2-butyne-1,4-diol, reaction with olefins gave the dienols only in low yields even in the presence of 2 equiv of magnesium oxide.

Introduction

The stereo- and regiospecific synthesis of conjugated dienes are of great importance in organic chemistry, as well as in their utilization in other reactions such as Diels-Alder reaction.¹ Vinylation of organometallic compounds with olefins by exchange reaction of palladium could be a promising method for the preparation of conjugated dienes,^{2,3} 1,4-dienes⁴ and aryl substituted olefins.⁵⁻⁷

We have recently reported that the reaction of (E)- β -alkenylboronic acids⁸ and highly hindered (E)- or (Z)- β -acetoxyvinylmercurials⁹ with olefins in the presence of a catalytic amount of palladium(II) salt and cupric chloride as a reoxidant for the palladium afforded the corresponding various functionalized conjugated dienes stereo- and regiospecifically. We now report the vinylation of (E)- β -chloro- γ -hydroxyvinylmercurials, readily obtainable by mercuriation of propargylic alcohols,^{10,11} with several functionalized olefins in the presence of catalytic amount of palladium(II) salt.

Results and Discussion

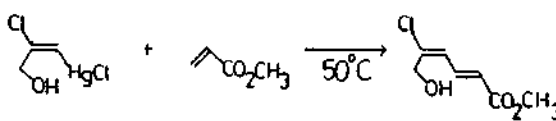
When we attempted to carry out the reaction of (E)-2-chloro-3-chloromercuri-2-propen-1-ol(**1**) with methyl acrylate in the presence of 10 mol % Li_2PdCl_4 and 2 equiv of cupric chloride in methanol at room temperature, we failed to obtain the expected (E,E)-2,4-dienol, and the starting vinylmercurial **1** was recovered. However, the reaction carried out at 50°C gave (E,E)-methyl 5-chloro-6-hydroxy-2,4-hexadienoate (**4**) in 65% yield (Table 1). We examined the effect of several different solvents on the rate of vinylation and the yield. Table 1 shows that the more polar solvents give faster reactions and higher yields of the vinyolated products.

We reasoned that the failure of the reaction at room

temperature might be due to the strong coordination of palladium chloride to the hydroxy group of vinylmercurial so that the reaction was no longer able to give rapid transmetallation with the mercurial moiety.¹¹ In order to solve this problem we have run the reaction of **1** with methyl acrylate in the presence of several inorganic bases, that were expected to more strongly coordinate with the hydroxy group, freeing the palladium for transmetallation (Table 2). Addition of 1 equiv of the inorganic base to the reaction mixture brought dramatically a rapid and clean vinylation at room temperature and the magnesium oxide bringing the best result.

(E)-2-Chloro-3-chloromercuri-2-propen-1-ol(**1**), (E)-3-chloro-4-chloromercuri-2-methyl-3-buten-2-ol(**2**) and (E)-2-chloro-3-chloromercuri-2-buten-1,4-diol(**3**) were reacted with olefins in the presence of 10 mol % Li_2PdCl_4 , 2 equiv of cupric chloride and 1 equiv of magnesium oxide in methanol at room temperature. (E,E)-2,4-Dienols were obtained stereospecifically. Results are summarized in Table 3.

Table 1. Effect of Solvents on Vinylation*



Solvent	Catalyst	Time, h	Yield ^a
Acetonitrile	Li_2PdCl_4	5	54
Methanol	Li_2PdCl_4	5	65
THF	Li_2PdCl_4	10	50
Benzene	PdCl_2	10	40

*3 mmol of (E)-2-chloro-3-chloromercuri-2-propen-1-ol, 3.5 mmol of methyl acrylate, 0.3 mmol of catalyst, 6 mmol of cupric chloride, 50°C, 30 ml of solvent. ^a% yield of isolated product.