ALPHA CARBOCATION STABILIZATION BY SILICON, GERMANIUM AND TIN

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Abstract: *The hydrolyses of a number of α-metalloidal vinyl ethers were found to undergo a rate-limiting protonation to produce α- silyl, germyl or stannyl carbocations. Comparative rate data leads to the ordering: C>Sn>Ge>Si>H, for the stabilization of such intermediates.*

For some time, we have had an interest in the role played by proximate metalloidal groups in the modification of normal alkene reactivity. Several of these studies have focused upon the synthesis of α-metalloidal vinyl ethers as precursors to acyl derivatives of silicon, germanium and tin.[1] In this Letter, we present a quantitative study of the kinetics of the hydrolysis process and its implication as to the ability of metalloidal substituents to stabilize an α-carbocation.

Methyl vinyl ether is well known to undergo *alpha* deprotonation with *t*-butyllithium in THF/C_5H_{12} solution to give α-methoxyvinyllithium[2] which is readily converted to the corresponding metalloidal compound.[1] In addition to our own studies, others have also found related intermediates to be excellent precursors of acylsilanes.[3]

M = Si, Ge, Sn
R = alkyl, aryl, vinyl
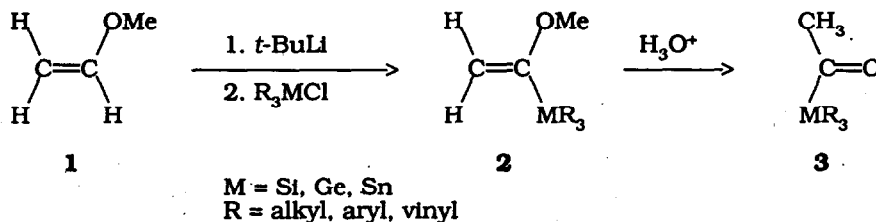
While the systematic kinetic studies of Eaborn[4] have demonstrated that *beta* metalloidal groups stabilize carbocations in the periodic order: C<Si<Ge<Sn<Pb, no comparable study has been carried out for systems which give *alpha* metalloidal carbocations. In fact, it is precisely this large stabilizing *beta* effect[5] of such metalloidal groups which has made the clean generation of the *alpha* metalloidal carbocations so difficult.[6] However, the extensive studies of Kresge and others,[7] established that a wide variety of vinyl ethers undergo hydrolysis with a slow protonation of the carbon-carbon double bond at the position *beta* to the alkoxy group, which, for our system, would give **4**, or its hydrate.[7f] Were this regioselectivity and kinetic behavior to also be found for our systems, it was felt that much could be learned regarding the extent of stabilization imparted to a carbocation. generated under solvolytic conditions, by α- silyl, germyl or stannyl groups.
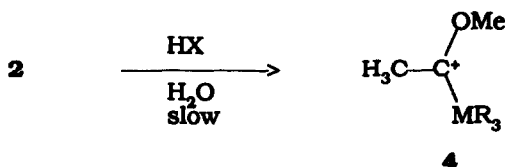
Vinyl ethers are systems for which changes in the nature of *alpha* substituents have a significant influence on the hydrolysis rates. General acid catalysis is observed. Also, typical values for k_H/k_D in aqueous solution range from 2-4 to higher values for carboxylic acid catalysis.[7] The hydrolytic conversion of **2** to **3** was examined in detail for the trimethyl series (**2a-c**) of the Si, Ge and Sn compounds as well as for the triphenyl series (**2d-f**). In each case, the starting ether, **2**, is smoothly converted to the corresponding acylmetallic compound cleanly and without detectable side reactions. The hydrolysis of these vinyl ethers was subjected to several of the experimental criteria expected for the A-S_E2 mechanism which is now generally accepted for these systems.[7,8] First, in all cases, at constant acid concentration, the hydrolyses show clean first-order kinetics in both the disappearance of **2** and in the appearance of **3**. Second, when the hydrolysis was carried out in deuterated solvents, the incorporation of a single deuterium atom in the product (**3**) was observed by ^{1}H NMR as a three line pattern (J = 2 Hz) in the 2.1 - 2.6 ppm region. Third, for **2c**, the reaction was carried out over an appropriate range of acid concentrations (ie. 2.43 ±0.03 x 10^{-3} to 2.43 ±0.03 x 10^{-2} M) and a precisely linear first-order dependence of the reaction rate upon acid concentration was observed. Fourth, the reaction exhibits large primary isotope effects (ie. k_H/k_D(28.5°C) = 5.6 [**2a**]; 6.1 [**2b**]; 6.7 [**2c**]) by comparison of the rates in 4:1 acetone-water *versus* the wholly deuterated solvent system. Moreover, these kinetic isotope effects diminish with increasing $\Delta G^{\ddagger}$, a result which agrees well with the behavior of other vinyl ethers in this range of reactivities.[7c]

The hydrolyses of the trimethyl metalloidal vinyl ethers was carried out over a range of temperatures in order to determine the activation parameters for the conversions (cf. Table 1).[8]

TABLE 1. ACTIVATION PARAMETERS FOR THE HYDROLYSES OF **2a-c** at 298°K.[a]

Compound	k(M^{-1} s^{-1})	E_a	log A	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
2a	0.242	23.0±0.9	16.2±0.2	22.4±0.9	13.6±3.0	18.3±0.9
2b	0.686	22.5±1.7	16.4±0.4	2..9±1.7	14.5±5.7	17.6±1.7
2c	3.55	23.5±1.0	17.7±0.2	22.9±1.0	20.5±3.3	16.8±1.0

[a] Data was obtained at [HCl]$_{total}$ = 2.43±0.03 x 10^{-2} M. in 4:1 acetone-water. Error estimates are based upon 2 standard deviations using least-square analyses of the log k vs 1/T plots (Range of T: **2a** 16-40°C; **2b** 18 -35.5°C; **2c** 14 - 28°C). Units are reported in kcal/mol for E_a, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ and in cal mol^{-1} deg^{-1} for $\Delta S^{\ddagger}$; all at 298°K.

The reactions followed clean first-order kinetics as determined by the smooth increase in the n->π^* (or σ->π^*) absorbance[9] with increasing time. The monitored wavelengths were chosen near the λ_{max} values for each product (**3a**: 370; **3b**: 380; **3c**: 390 nm). Positive $\Delta S^{\ddagger}$ values have been observed for the hydrolysis of simple vinyl ethers under these conditions.[7b] This, coupled with the larger kinetic isotope effects (*vide ultra*) observed for **2**, suggests that acetone is involved in the proton transfer to form **4** rather than simply a pure aquated hydronium ion.[10] Kinetically, our data appeared to position **2a-c** between **1** and α-alkyl vinyl ethers.[7] Since the UV technique used in the above study was not appropriate for this solvent system for these non-metalloidal compounds, we chose to obtain relative rate data in deuterated solvents with the aid of ^{1}H NMR.

In 4:1 $(CD_3)_2CO/D_2O$ containing varying concentrations of DBr catalysis, these ethers were examined, at 33°C, in groups based upon their reactivities, namely, 1) **1** vs **2a**, 2) **2a**, **2b** and **2c**, and 3) **2c** vs the α-t-butyl compound (**2g**). These comparative data are summarized in Table 2.

Table 2. DEUTEROLYSES OF *ALPHA*-SUBSTITUTED VINYL ETHERS.[a]

| MR_3	=	H (**1**)	$SiMe_3$ (**2a**)	$GeMe_3$ (**2b**)	$SnMe_3$ (**2c**)	CMe_3 (**2g**)
k_{rel}	=	1.0	1.8	4.3	12	100

[a]For the **2a-c** and **2c** vs **2g** series, 0.2 mmol of the liquid ether was injected into a septum-sealed NMR tube containing the thermally equilibrated, standardized hydrolysis mixture (0.5 mL) under a N_2 atmosphere. For the **1** vs **2a** comparison: To these compounds (0.2 mmol) in $(CD_3)_2CO$ (0.4 mL) was added standardized acid solution in D_2O (0.100 mL). The methoxy signals in **2** and those in MeOD were integrated with time. Each run was performed in duplicate and gave precisely linear plots for ln $[2]/[2_{initial}]$ vs t for at least 3 half-lives.

A further comparison reveals that the above relative rates of the trimethyl (ie. **2a-c** = 1 : 2.4 : 6.7) is quite similar to the corresponding triphenyl (viz. **2d-f**) compounds (ie. 1 : 2.3 : 5.3) in a $C_6D_6/(CD_3)_2CO/D_2O$ (5:24:1) solvent system. Moreover, direct comparison of a 1:1 mixture of **2a** and **2d** under these conditions reveals that the trimethylsilyl derivative hydrolyzes 30 times faster than its triphenyl counterpart. Unfortunately, the trimethyllead derivative of **2** did not form the acetyl compound cleanly under these dilute acid (ca. 0.02 M HCl) conditions. Apparently cleavage of either this product or the starting vinyl ether to produce chlorotrimethyllead is a competitive process. Previous studies[1c] on the conversion of the butadienyl derivatives (**5**) to the corresponding monodeuterated crotonylmetallanes (**6**) also revealed that they hydrolyze slower than for the corresponding **2a-c** series. The same relative order, namely **5a**<**5b**<**5c**, was observed, but with attenuated differences in the relative rates (ie. 1.0 : 1.6 : 2.9). This finding is consistent with the more remote site of deuteration with respect to the oxygen and metalloidal substitution.
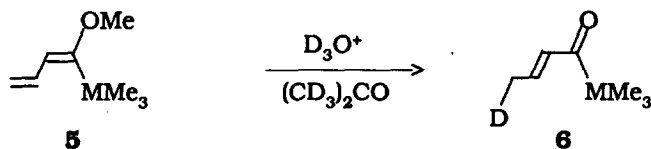
Other metalloidal systems have been studied (**7-9**)[1] and their hydrolyses were found to be complicated by regioisomeric protonation in the case of **7** and partial protiodestannylation in the case of **8c**. However, the silicon derivatives (ie. **7-9a**) do exhibit smooth first-order kinetics in each case. Hence, we can approximate the reactivity as **2a** > **7a** > **2d** ~ **5a** ~ **9a** > **8a**. Moreover, the relative order, namely Si < Ge < Sn, remains constant as we reported earlier,[1c] in each case studied, an ordering which has also more recently been inferred from IR data.[11]

The present study addresses a fundamental question raised by the early studies of Whitmore and Sommer[12] as to the relative stabilizing effect of silyl, and more generally, Group 4 metalloidal substituents on an adjacent cation under solvolytic conditions. Attempts to generate simple α-silyl carbocations are normally thwarted by rearrangements or other mechanistic ambiguities. Thus, the most information on the role played by metalloidal groups has come from the more remote ethynyl or aryl derivatives where, for example in the latter case, the trimethylsilyl group can vary from weakly-electron withdrawing to electron-donating, depending upon the solvent and the

7   **8**   **9**
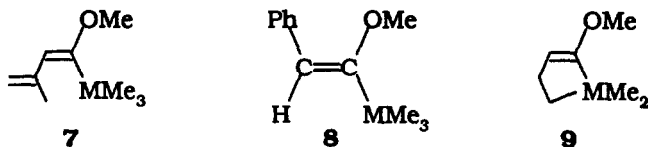
particular reaction under study.[13] Spectroscopic methods as well as calculations suggest that silyl groups can stabilize an α-carbocation.[14] Our systems, which undergo undergo clean, quantitative reactions without rearrangement and which are wholly in accord with the firm mechanistic criteria established for the analogous non-metalloidal vinyl ethers, would appear to be particularly well suited for determining the role of these metalloidal substituents in α-carbocation stabilization. Moreover, as for t-Bu and SiMe$_3$, it seems reasonable to assume that steric hindrance to solvation[13b] of the transition states leading to **4** would be present in our acetone-water system for the analogous germanium and tin compounds as well. Yet, despite this hindrance, all of the compounds, **2a-c** as well as the t-Bu derivative, **2g**, are more reactive than the parent vinyl ether, **1**. Thus, the order of stabilization imparted to **4**, over and above the major contribution of the methoxy group, by the α substituent, namely H < SiMe$_3$ < GeMe$_3$ < SnMe$_3$ < CMe$_3$, can be viewed as a large +R (σ-π hyperconjugation[15]) only for the t-butyl derivative, **2g**. The metalloidal compounds with their longer C-M bond length fail to provide this stabilization[6b] and an increasing +I (field/inductive) effect with diminished electronegativity[16] (ie. C—>Sn) results in a minor stabilization of **4** by the metalloidal groups when compared to a hydrogen atom.[17]

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17. *Note added in proof.* Implicit in our interpretation of these data are the assumptions that the effect of the α group is not overwhelmed by the oxygen and that, despite the differing positions of the transition states leading to **4**, the data are still reflective of their effect in **4**.[7] We thank the referee for his suggestion that this be mentioned.