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Electrochemical Approach to Germenium and Silicenium Ions

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The reduction potentials for carbonium, silicenium, and germenium ions were determined by cyclic voltammetry of neutral precursor compounds. The reduction potential shifted to the negative direction as the center element changed from C to Ge.

Synthesis and identification of silicenium ions and germenium ions have been the current topics in organosilicon and organogermanium chemistry. In spite of all previous attempts, the presence of such ions is still in question.[1)] Among such attempts, electrochemical generations of $Me_3Si^+(NCCH_3)_n$[2)] and Ph_3Ge^+[3)] have been suggested. However, they are not generally accepted since scientific data, which support their existence, are insufficient. Accordingly, the authors report here more data upon the electrochemically generated species and discuss their characteristics.

Commercially available triphenylmethane and 2-phenylpropane were purified and used for experiments. Silicon and germanium compounds were synthesized and identified by the conventional manners.

Cyclic voltammetry was performed by using Pt electrodes as the working and counter electrodes and a Ag electrode as the quasi reference electrode. All oxidation and reduction potentials were determined against the redox potentials of ferrocene (Fc) and ferricinium ion (Fc^+). The supporting electrolyte was tetrabutylammonium perchlorate (TBAP).

Oxidation of Ph_3CH gives Ph_3C^+.[4)] In the cyclic voltammogram, oxidation and reduction peaks are located at 1.81 V ($E^{ox}_{p/2}$) and -0.04 V ($E^{red}_{p/2}$), respectively. The reduction peak is observed only when Ph_3CH is oxidized in the previous scan. Therefore, the reduction peak is assigned to that due to the reduction of Ph_3C^+. This is confirmed by the coincidence of the $E^{red}_{p/2}$ value with the values reported for reduction of Ph_3C^+.[5,6)]

All cyclic voltammograms for the precursors listed in Table 1, showed the same behavior. The electrochemical oxidation of the precursor will occur as shown by Eqs. 1 and 2. Though only Ph_3C^+ is stable under experi-

Table 1. Oxidation and reduction potentials ($E^{ox}_{p/2}$:Peak 1, $E^{red}_{p/2}$:Peak 2) in CH_3CN

Precursor	Cation	$E^{ox}_{p/2}$ / V vs. Fc/Fc^+	$E^{red}_{p/2}$ / V vs. Fc/Fc^+
Ph_3CH	Ph_3C^+	1.81 ± 0.03	-0.04 ± 0.05
$PhMe_2CH$	$PhMe_2C^+$	1.89 ± 0.03	-0.20 ± 0.05
$Ph_3SiSiMe_3$	Ph_3Si^+	1.29 ± 0.03	-0.30 ± 0.10
$(PhMe_2Si)_2$	$PhMe_2Si^+$	1.26 ± 0.03	-0.51 ± 0.10
$(Me_3Si)_2$	Me_3Si^+	1.36 ± 0.03	-0.59 ± 0.10
$Ph_3GeGeMe_3$	Ph_3Ge^+	1.16 ± 0.03	-0.69 ± 0.10
$(Ph_2MeGe)_2$	Ph_2MeGe^+	1.20 ± 0.03	-0.92 ± 0.10
$(PhMe_2Ge)_2$	$PhMe_2Ge^+$	1.24 ± 0.03	----------[a]
$(Me_3Ge)_2$	Me_3Ge^+	1.28 ± 0.03	----------[a]

a) The potential was not able to be determined because the life time of the intermediate was too short.

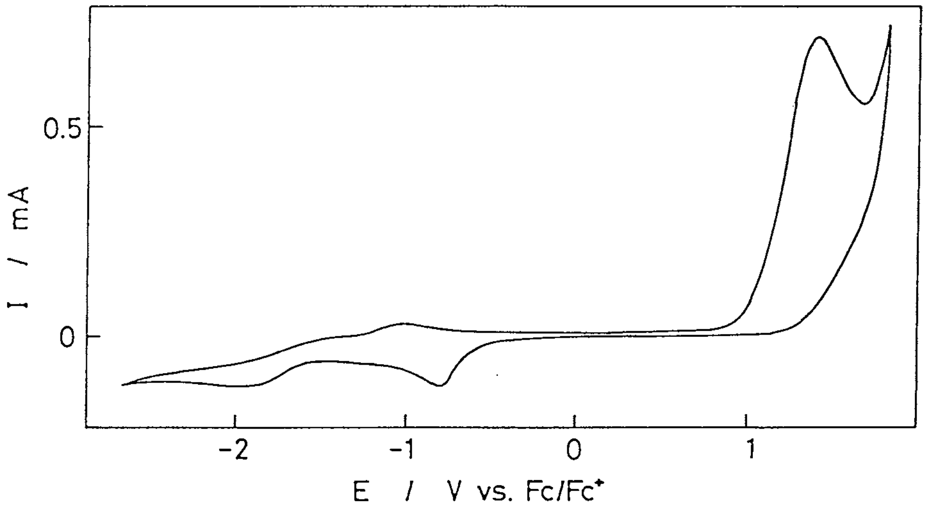

Fig. 1. A cyclic voltammogram for $Ph_3GeGeMe_3$ in CH_3CN.

$$R_3CH \xrightarrow{-2e} R_3C^+ + H^+ \quad (1)$$

$$R_3E\text{-}ER'_3 \xrightarrow{-2e} R_3E^+ + R'_3E^+ \quad (2)$$

mental conditions, the other cationic species had life times long enough to give the reproducible reduction peaks.[7)] However, it should be noted that the $E^{red}_{p/2}$ values have rather large experimental errors because the peaks are broad and sensitive to the residual water in the electrolyte. Neverthe-

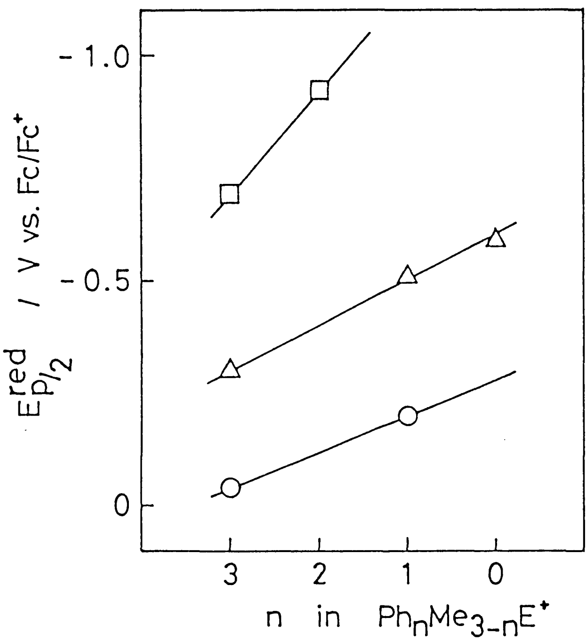

Fig. 2. The $E^{red}_{p/2}$ values for I(R_3C^+) (○), I(R_3Si^+) (△), and I(R_3Ge^+) (□) as a function of n in $Ph_nMe_{3-n}E^+$.

less it is clear that the $E^{red}_{p/2}$ value shifts to the negative direction as the precursor changes from Ph_3CH through $Ph_3SiSiMe_3$ to $Ph_3GeGeMe_3$.

A cyclic voltammogram for $Ph_3GeGeMe_3$ is shown in Fig. 1.[8] It is oxidized at 1.16 V. The intermediate produced by the oxidation is reduced at -0.69 V. The $E^{red}_{p/2}$ value observed here is different from that for synthesized $Ph_3GeOClO_3$ reported by Boczkowski et al.[3] Since Ph_3GeClO_3 is reported to be stable, the cationic intermediate observed here should not be $Ph_3GeOClO_3$.

In Fig. 2, the substituent effect is clearly observed. On replacement of a phenyl group by a methyl group, the $E^{red}_{p/2}$ value for R_3C^+ shifted by -0.08 V, while those values for I(R_3Si^+) and I(R_3Ge^+) were -0.10 and -0.32 V, respectively, where the intermediate species are abbreviated as I(R_3C^+), I(R_3Si^+), and I(R_3Ge^+). Electron-donating nature of methyl group was more largely reflected on the $E^{red}_{p/2}$ values for I(R_3Si^+) and I(R_3Ge^+). Extrapolation of the line for I(R_3Ge^+) gave the $E^{red}_{p/2}$ value of -1.15 V for I($PhMe_2Ge^+$) and -1.38 V for I(Me_3Ge^+).

As well studied by Breslow,[5] Feldman,[9] and Bank,[10] and their coworkers, reduction potentials of the carbocations can be recognized as redox potentials for the reversible change between cations and radicals. Therefore, if I(R_3Si^+)'s and I(R_3Ge^+)'s are not solvated but free, the $E^{red}_{p/2}$ values in Table 1 indicate that the corresponding radicals should have very strong electron donating properties. This is in good agreement with the recent reports on reactions of organosilicon and organogermanium compounds, in which silyl and germyl radicals were thought to be the key reaction intermediates.[11]

Boberski et al. reported that a plot of the reciprocal of the ratio of Peak 2 to Peak 1 as a function of elapsed time between Peak 1 and Peak 2 makes a good straight line.[2] Such plots for the precursor compounds revealed that the relative life time of the cation becomes shorter in the following order : I(Ph_3Si^+) > I($PhMe_2Si^+$) > I(Me_3Si^+) > I(Ph_3Ge^+) > I(Ph_2MeGe^+) > I($PhMe_2Ge^+$) > I(Me_3Ge^+). The followings should be noted.

(1) I(R_3Si^+) survives longer than I(R_3Ge^+). Considering a carbocation having a longer life time, the life time of the cation becomes shorter as the center element changes from C to Ge. (2) Cations with three phenyl groups have the longest life time compared with those with less phenyl groups. (3) The cations with their $E_{p/2}^{red}$ values at less negative potentials, have longer life times.

In the present paper, there obtained no clear evidence indicating the intermediate cations to be free. However, the data for carbon, silicon, and germanium species, obtained with the same method under the same conditions, will be a good guideline for the future experiments. It should be noted that the $E_{p/2}^{red}$ values for solvated ions are still important as fundamental data in estimating ΔG for various kinds of reactions.

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7) These intermediate species are not necessarrily free cations. Silicenium and germenium ions may be coordinated with the solvent.

8) $(Ph_3Si)_2$ and $(Ph_3Ge)_2$ are not suitable precursors because their solubilities in the electrolyte solution are too low for the measurement. The $E_{p/2}^{red}$ values for $Ph_3SiSiMe_3$ and $Ph_3GeGeMe_3$ can be clearly explained from Fig. 2 as those for I(Ph_3Si^+) and I(Ph_3Ge^+) but not for I(Me_3Si^+) and I(Me_3Ge^+).

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