Oxidation Potentials of Electrochemically Accumulated Anions and Prediction of Them by Theoretical Calculation

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13 compounds including 6 germanes were examined as precursors for the electrochemical anion accumulation in dimethylformamide-tetrabutylammonium tetrafluoroborate system at -50°C . Accumulation of 9 anions was confirmed by measuring their oxidation potentials (That of 5 anions was also confirmed by NMR). Oxidation potentials of the 9 anions were determined by cyclic voltammetry. It was concluded that the anions can be accumulated in the system when their oxidation potentials are less negative than -1.26 V vs. SCE . The prediction of the oxidation potentials and thus the accumulation of the anions were successfully carried out by calculating the HOMO energy levels of the model compounds with K counter cations at DFT - B3LYP (6-31G *) level.

Key Words : Electrochemically Generated Anion, Electro-reduction, Oxidation Potential, HOMO Energy Level, Calculation

1 Introduction

Since 1990, the electrochemical methods that utilize the accumulation of the electrochemically generated active species (anions, radicals, and cations) have attracted attention of many researchers.¹⁻²¹⁾ It has been pointed out that such methods have the following advantages.^{10,12,18)} (1) A wide choice of compounds (precursors) is possible because precursors are electrolyzed in the absence of reaction substrates. (2) The methods can be applied to a variety of products because electrolysis of products is avoided. (3) Accumulated species can be used in portions and they are suitable for combinatorial synthesis. (4) Accumulated species can be stocked, transported, and used as conventional reagents without electrochemical set-ups. However, still limited numbers of electrochemically generated active species have been accumulated. More studies on the structural requirements and experimental conditions are required in order to expand the chemistry of these new methods.

Among such active species, anions are discussed in this paper. As well known, fluorenyl anion and its related anions can be obtained electrochemically in various solvents.³⁾ However, not many kinds of anions are stable under such conditions. In 1990, Fuchigami and his co-workers successfully accumulated the well known stable triphenylmethyl anion in dimethylformamide(DMF)-tetrabutylammonium tetrafluoroborate(TBATFB) at -50°C .¹⁾ At that time, they were not aware of the unique character of the solvent-supporting electrolyte system. Later, accumulations of various carbanions, germynyl anions, and stannyl anions in the system were reported by Okano and his co-workers.²⁻¹⁰⁾ It is now clear that the solvent-supporting electrolyte system is a unique system that can stabilize various kinds of anions at low temperatures. In the DMF-TBATFB system, the number of anions that can be generated and accumulated electrochemically is

gradually increasing. However, the requirements that the anions should meet for their accumulation are still not clear.

On the other hand, it has been known that (1) generally speaking, anions sometimes show one electron transfer reactions,^{22,23)} and (2) in case of electrochemically accumulated anions, one electron transfer to the counter cation has been strongly suggested during the decomposition of them because formation of trialkylamine is observed.⁵⁾

Therefore, it is important to know if there is a relationship between the electron donating ability of the anions and stability (and also reactivity) of them. The first object of this work is to know the range of electron donating ability of the anions as a function of oxidation potential and to clarify the fact that electron donating ability determines the stability of the anions. The second object of this work is to establish a method to predict the oxidation potentials of the anions, and to make it possible to predict the possibility of electrochemical anion accumulation from their chemical structures.

2 Experimental

2.1 Materials

The 13 compounds shown in Fig. 1 were examined as precursors (C1 - C7 and Ge1 - Ge4, Ge6, Ge7) to generate the anions (C1-a - C7-a and Ge1-a - Ge4-a, Ge6-a, Ge7-a) electrochemically according to Eq. 1. Reaction of the accumulated anions with iodomethane as shown in Eq. 2 was also examined.

Fig. 1 Precursors examined to generate anions.

The following 7 precursors were synthesized in our laboratory and identified by comparing their physical properties with those reported in the literature. (1,1-diphenylethane (MePh₂CH, C4) : b.p. 81-83 °C/0.40 Torr,²⁴) triphenylgermane (Ph₃GeH, Ge1) : m.p. 43-44 °C,²⁵) methylphenylgermane (MePh₂GeH, Ge4) : b.p. 73-74 °C/0.12 Torr,²⁶) dimethylphenylgermane (Me₂PhGeH, Ge7) : b.p. 73-75 °C/40 Torr,²⁷) diphenylgermane (Ph₂GeH₂, Ge2) : b.p. 73-74 °C/0.15 Torr,²⁸) ditolylgermane (Tol₂GeH₂, Ge3) : b.p. 101-103 °C/0.18 Torr,²⁸) methylphenylgermane (MePhGeH₂, Ge6) : b.p. 67-69 °C/41 Torr,²⁶) The other 6 precursors were commercially available and they were used after purification either by distillation or recrystallization. (triphenylmethane (Ph₃CH, C1), diphenylmethane (Ph₂CH₂, C2), ditolylmethane (Tol₂CH₂, C3), and ethylbenzene (MePhCH₂, C6) : Tokyo Chemical Industry Co., Ltd., cumene (Me₂PhCH, C7) and toluene (PhCH₃, C5) : Wako Pure Chemical Industries, Ltd.)

The reaction products of the anions with iodomethane were identified and quantitatively analyzed using the following standard compounds. 8 compounds were synthesized in our laboratory and 7 compounds were identified by comparing their physical properties with those reported in the literature. 1,1,1-triphenylethane (MePh₃C, C1-Me) : m.p. 94-95 °C,²⁹) MePh₂CH (C2-Me) : See above (C4), methyltriphenylgermane (MePh₃Ge, Ge1-Me) : m.p. 70-72 °C,³⁰) dimethyldiphenylgermane (Me₂Ph₂Ge, Ge4-Me) : b.p. 79-81 °C/0.08 Torr,³¹) trimethylphenylgermane (Me₃PhGe, Ge7-Me) : b.p. 93-94 °C/194 Torr,³²) MePh₂GeH (Ge2-Me) : See above (Ge4), Me₂PhGeH (Ge6-Me) : See above (Ge7). Methyl ditolylgermane (MeTol₂GeH, Ge3-Me) was identified by ¹H NMR (in CDCl₃, δ (vs. TMS) = 7.39 (d, 4H), 7.16 (d, 4H), 5.03 (q, 1H), 2.33 (s, 6H), 0.68 (d, 3H)). The other 4 compounds were commercially available. Me₂PhCH (C6-Me) : See above (C7), MePhCH₂ (C5-Me) : See above (C6), 2,2-diphenylpropane (Me₂Ph₂C, C4-Me) : SIGMA-ALDRICH, Inc., and tert-butylbenzene (Me₃PhC, C7-Me) : Tokyo Chemical Industry Co., Ltd.

The solvent, N,N-dimethylformamide (DMF) purchased from Wako Pure Chemical Industries, Ltd., was dried over CaH₂ and distilled under nitrogen atmosphere before use. Tetrabutylammonium tetrafluoroborate (TBATFB) purchased from Tokyo Chemical Industry Co., Ltd. was used as the supporting electrolyte after recrystallization in dry ethyl acetate and pentane and drying under vacuum.

2. 2 Measurement of the oxidation potentials

The determination of oxidation potentials was carried out according to the recently reported procedure using a three-compartment cell.²⁾ First, an anion was accumulated in the center compartment of the three-compartment cell by reducing (1 F mol⁻¹) the corresponding precursor (typically 0.1 mol dm⁻³) in DMF in the presence of 0.3 mol dm⁻³ TBATFB at -50 °C.

Then, cyclic voltammetry was carried out with a newly introduced fresh platinum disc working electrode (area : ca. 0.02 cm²), a Ag/Ag⁺ reference electrode, and a counter electrode. The surface of the working electrode was carefully polished with alumina prior to use. The oxidation potentials were first measured against ferrocene/ferrocenium in DMF, and then converted to the values in V vs. SCE.

2. 3 Reaction with iodomethane

Using a two-compartment cell, the anion was accumulated in the catholyte by electrolysis of 1 F mol⁻¹. Then, cold iodomethane (4 equivalent moles to the precursor, -50 °C) was introduced in the anion solution over 2 min, and the reaction was carried out at -50 °C for 1 h.

After extraction with ether, the methylated compounds in the extracted solution were quantitatively analyzed by gas chromatography (conditions : SHIMADZU GC-8APF / SHIMADZU Silicone SE-30 packed column 3 mmφ × 1800 mm, flow 30 ml min⁻¹, heat rate 16 °C min⁻¹/50-280 °C) using the internal standard method.

2. 4 Calculation on the model compounds

In order to estimate HOMO energy levels (E_{HOMO}) of the anions, those of anion model compounds were calculated at DFT - B3LYP (6-31G*) level using Spartan '06 (Wavefunction, Inc.).

Li, Na, and K salts of the anions were employed as the model compounds because the experimentally obtained ammonium cation is not suitable for the theoretical calculations for it has flexible alkyl chains.

3 Results and Discussion

3. 1 The oxidation potentials of the accumulated anions

Upon electro-reduction of one of the 13 examined precursors listed in Table 1, colored species accumulated in the catholyte. The examination of the resulting catholyte solution by NMR proved the accumulation of Ge1-a,⁷⁾ Ge2-a,²⁾ Ge4-a,⁸⁾ Ge7-a,⁸⁾ and C1-a⁵⁾ as already reported. In case of the other anions, the transfer of the anion solution was unsuccessful because of their low stability.

In order to know the accumulation of the anions in the remaining cases, the existence of chemical species with highly electron-donating property was examined by cyclic voltammetry in the colored solutions, because as

Table 1 The accumulation of the anions, the oxidation potentials, and the reaction yields.

Precursor	Anion	Anion Abbrev.	Color at -50°C	E_{ox} / V vs. SCE	Products (-Me) ^{a)} Yield ^{b)} / %
Me_2PhCH	$(\text{Me}_2\text{PhC})^-$ ^{c)}	C7-a	(Yellow) ^{c)}	--- ^{e)}	--- ^{f)} (Me_3PhC)
MePhCH_2	$(\text{HMePhC})^-$ ^{c)}	C6-a	(Yellow) ^{c)}	--- ^{e)}	--- ^{f)} (Me_2PhCH)
PhCH_3	$(\text{H}_2\text{PhC})^-$ ^{c)}	C5-a	(Yellow) ^{c)}	--- ^{e)}	--- ^{f)} (MePhCH_2)
MePh_2CH	$(\text{MePh}_2\text{C})^-$ ^{d)}	C4-a	(Reddish Brown) ^{d)}	--- ^{e)}	Trace ($\text{Me}_2\text{Ph}_2\text{C}$)
Tol_2CH_2	HTol_2C^-	C3-a	Brown	-1.26	--- ^{g)} (MeTol_2CH)
Ph_2CH_2	HPh_2C^-	C2-a	Brown	-1.17	12 (MePh_2CH)
Ph_3CH	Ph_3C^-	C1-a	Red	-1.15	26 (MePh_3C)
Me_2PhGeH	Me_2PhGe^-	Ge7-a	Yellow	-0.98	5 (Me_3PhGe)
MePh_2GeH	MePh_2Ge^-	Ge4-a	Yellow	-0.86	24 ($\text{Me}_2\text{Ph}_2\text{Ge}$)
MePhGeH_2	HMePhGe^-	Ge6-a	Yellow	-0.74	27 (Me_2PhGeH)
Ph_3GeH	Ph_3Ge^-	Ge1-a	Yellow	-0.72	33 (MePh_3Ge)
Tol_2GeH_2	HTol_2Ge^-	Ge3-a	Yellow	-0.70	42 (MeTol_2GeH)
Ph_2GeH_2	HPh_2Ge^-	Ge2-a	Yellow	-0.66	24 (MePh_2GeH)

a) Methylated product obtained by the reaction with iodomethane. b) GC yields (electrolysis : 1 F mol⁻¹). c) The anion was not accumulated. d) Not confirmed. e) No oxidation peak in the expected potential region. f) Not detected. g) A standard sample was not available. A very small peak was observed at the expected retention time on the gas chromatogram.

Fig. 2 A cyclic voltammogram obtained in the accumulated MePh_2Ge^- solution.

already discussed in the introduction part, anions show high electron-donating tendency in general.

In 9 solutions among the examined 13 solutions, cyclic voltammograms that indicate the existence of chemical species with high electron donating property were obtained. The oxidation potentials listed in Table 1 were determined as follows. Figure. 2 is an example of a cyclic voltammogram obtained in MePh_2Ge^- solution. The oxidation wave was attributed to the oxidation of the anion to the radical shown in Eq. 3. No reduction wave attributable to the reduction of the radical to the anion as shown in Eq. 4 was observed. Dimerization of the radical species shown in Eq. 5 (or reactions of them with the solvent or the supporting electrolyte) may be the reason for the absence of the reduction wave. Onset oxidation potentials were employed as the oxidation potential because the re-reduction wave from the radical to the anion (Eq. 4) was observed only in case of Ph_3C^- . On Fig. 2, the onset oxidation potential was determined as -0.86

V vs. SCE. It should be noted that such onset oxidation potentials are usually very close to the oxidation-reduction potentials. Thus determined oxidation potentials are listed in Table 1. The obtained oxidation potential of Ph_3C^- , -1.15 V vs. SCE, and that of HPh_2C^- , -1.17 V vs. SCE, agreed very well with the reported oxidation peak potentials, -1.13 V vs. SCE and -1.17 V vs. SCE for the anions with Li^+ counter cations in HMPA/THF, respectively.³³⁾ That of Ph_3Ge^- , -0.72 V vs. SCE, agreed well with that of -0.78 V vs. SCE reported for the anion with $\text{K}^+/\text{Bu}_4\text{N}^+$ counter cation in DMSO (read from the reported linear sweep voltammogram).³⁴⁾ Also that of Me_2PhGe^- , -0.98 V vs. SCE, agreed with that of -1.09 V vs. SCE in HMPA for the anion with Li^+ counter cation (read from the reported cyclic voltammogram).³⁵⁾ Considering the electron donating property of methyl group, the order of the obtained oxidation potentials seemed reasonable.

It was found that germyl anions have low electron donating property compared to carbanions because the germyl anions showed their oxidation potentials at 0.5 to 0.6 V less negative potentials. Such conclusion seems reasonable considering the much larger size of germanium compared to carbon.

It was concluded that the 9 anions listed in Table 1 can be generated and accumulated electrochemically (This conclusion is further confirmed later by the reaction with iodomethane and also by the linear relationship

between the oxidation potentials and the calculated E_{HOMO} s.). The anions in parenthesis are those not obtained. Finally, it was concluded that anions can be accumulated when their oxidation potentials are less negative than -1.26 V vs. SCE.

3.2 Prediction of the Oxidation Potentials

In case of neutral compounds, the linear relationships between the oxidation potentials and HOMO energy levels (evaluated by ionization potential) have been pointed out by the early researchers.^{36,37} If the similar linear relationship exists between the oxidation potential of the anions and the calculated HOMO energy levels (E_{HOMO}), that enables prediction of oxidation potentials by input of molecular structures and calculations. Furthermore, on the basis of the results obtained in 3.1, possibility of accumulation can be predicted.

In order to calculate the E_{HOMO} s of the anions, Li, Na, and K salts were employed as the model compounds because the experimentally obtained anions with tetrabutylammonium cations are not suitable for calculation since tetrabutylammonium cation has flexible chains. The calculated E_{HOMO} s are summarized in Table 2. In all the cases, the E_{HOMO} s of the germyl anions appeared at lower energy levels compared to those of the carbanions.

Relationships between the oxidation potentials and the calculated E_{HOMO} s are shown in Fig. 3. In case of K salts, a linear relationship was obtained. It seems reasonable considering K is the largest among the three metals and the closest to the experimentally used tetrabutylammonium cation.

In conclusion, the oxidation potentials of the electrochemically accumulated anions can be predicted by the calculation of E_{HOMO} on their model compounds with K cations. Furthermore, considering the conclusion in 3.1, it is possible to predict the possibility of an anion accumulation from its chemical structure. Anions can be accumulated when the E_{HOMO} s of their model compounds with

K counter cations are lower than *ca.* -3.39 eV. They can not be accumulated when their $E_{\text{HOMO}} > \text{ca. } -3.25$ eV. (Intermediate region exists between -3.38 eV and -3.26 eV.) Here established calculation method will help many researchers because the calculation of HOMO energy levels can be carried out rather easily using the commercially available calculation softwares.

3.3 Reaction with iodomethane

Reaction of the accumulated anions with iodomethane gave the corresponding methylated products in all the cases where the anion was accumulated. Typical yields with 1 F mol^{-1} electrolysis are listed in Table 1 while

Table 2 The calculated HOMO energy levels (E_{HOMO}) of the model compounds.

Anion	Anion Abbrev.	HOMO Energy Level / eV		
		-Li	-Na	-K
(Me ₂ PhC ⁻)	C7-a	-3.80	-3.44	-3.11
(HMePhC ⁻)	C6-a	-3.97	-3.59	-3.17
(H ₂ PhC ⁻)	C5-a	-4.08	-3.85	-3.32
(MePh ₂ C ⁻)	C4-a	-3.84	-3.47	-3.35
HTol ₂ C ⁻	C3-a	-3.91	-3.48	-3.29
HPh ₂ C ⁻	C2-a	-4.05	-3.60	-3.40
Ph ₃ C ⁻	C1-a	-3.88	-3.56	-3.39
Me ₂ PhGe ⁻	Ge7-a	-4.72	-4.51	-3.84
MePh ₂ Ge ⁻	Ge4-a	-4.85	-4.63	-4.06
HMePhGe ⁻	Ge6-a	-4.90	-4.65	-3.99
Ph ₃ Ge ⁻	Ge1-a	-4.95	-4.73	-4.25
HTol ₂ Ge ⁻	Ge3-a	-4.90	-4.69	-4.16
HPh ₂ Ge ⁻	Ge2-a	-5.01	-4.77	-4.24

Fig. 3 Relationships between the oxidation potentials obtained in experiments and the HOMO energy levels obtained by DFT calculation on the model compounds with Li(●), Na(■), and K(◆) counter cations.

they varied considerably experiment to experiment. In Table 1, a tendency that the anions with high electron donating property show low yields is seen in both cases of the germyl anions and carbanions.

In order to know one of the factors that determines the yields, C1-a, C2-a, and C3-a were studied carefully. As easily understood, such yields depend on both Eq. 1 and Eq. 2. In case of chemically prepared anions, the yields of anions are evaluated by the reaction with D₂O using ¹H NMR. However, such determination was not successful in case of the electrochemically accumulated anions. One of the reasons for such failure seemed the difficulty of reaction at -50 °C where D₂O freezes. In order to avoid such difficulty, deuterated methanol (CH₃OD) was used instead of D₂O. However, reliable data were still not obtained. Finally, oxidation currents in the anion solutions were employed to roughly evaluate the anion concentration. Oxidation currents were carefully measured repeatedly under the conditions same as Fig. 2. Typically such current was 1.47 mA cm⁻² for C1-a, 0.83 mA cm⁻² for C2-a, and 0.06 mA cm⁻² for C3-a. (Such difference in current efficiency is often observed in electro-organic reactions.) Therefore, it was concluded that the total reaction yields strongly depend on the anion yield in Eq. 1. (Dependence on the reaction yield in Eq. 2 is not clear).

4 Conclusion

Oxidation potentials of various carbon and germanium centered anions were determined successfully. By analyzing the data, it was clarified that anions can be generated and accumulated in DMF-TBATFB system at -50 °C, when their oxidation potentials are less negative than -1.26 V vs. SCE. A linear relationship was observed between the oxidation potentials of the anions and HOMO energy levels of the model compounds calculated by DFT method. Possibility of accumulation can be predicted from the chemical structure. These results will help the expansion of chemistry using the electrochemically accumulated anions and the other active species.

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