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The Electrochemical Behavior of Mononitrophenyltrimethylsilanes and 2,4-Dinitrophenyltrimethylsilane

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Synopsis. The CV data for *o*-, *m*-, and *p*-nitrophenyltrimethylsilanes and 2,4-dinitrophenyltrimethylsilane revealed that the former three show E_{pc} slightly more anodic than the corresponding nitrotoluenes; the latter shows a third peak (O_3) together with two successive reversible couples, while the methyl analogue exhibits no peak corresponding to O_3, but shows extremely weak O_1. The behavior of these silyl compounds are interpreted in terms of less electron-donating nature of trimethylsilyl group and (p-d)π bonding between the siliicon and benzene ring.

To date only a few reports have appeared on the study of the electrochemical behavior of organosilicon compounds by polarography,[1,2] and controlled potential electrolysis in non-aqueous solutions.[3,4] Recently, Allred and co-worker have reported on the electrochemical reduction of chloropermethylpolysilanes by means of cyclic voltammetry (CV) and discussed the effect of chain length of the polysilanes on the reduction potentials.[5] It is interesting to investigate by the CV technique the electrochemical behaviors for other types of silicon compounds which contain at least one of electroactive groups. The present study was undertaken to examine the substituent effect on reduction-oxidation potentials and electron transfer processes for *o*-, *m*-, and *p*-nitrophenyltrimethylsilanes and 2,4-dinitrophenyltrimethylsilane.

Results and Discussion

o-, m-, *and* p-*Nitrophenyltrimethylsilanes.* In Table 1, the CV data are listed to compare mononitrophenyltrimethylsilanes with nitrotoluenes. The peak potentials E_{pc}, E_{pa}, and $E_{p1/2}$, for the silyl compounds are both slightly more anodic than those of the corresponding toluene derivatives. This may be attributable to the polar effect of substituent attached to the nitrophenyl group, less electron-donating trimethylsilyl substituent compared with methyl group requires lower reduction potentials as shown by Hammett σ constants.[6]

TABLE 1. THE CV DATA OF NITROPHENYLTRIMETHYLSILANES AND NITROTOLUENES[a]

Compound	E_{pc} (V)	E_{pa} (V)	$E_{p1/2}$ (V)	i_{pa}/i_{pc}
o-$MeC_6H_4NO_2$	−1.66	−0.80	−1.23	1.0
o-$Me_3SiC_6H_4NO_2$	−1.62	−0.68	−1.14	0.9
m-$MeC_6H_4NO_2$	−1.52	−0.76	−1.13	1.0
m-$Me_3SiC_6H_4NO_2$	−1.50	−0.76	−1.11	1.0
p-$MeC_6H_4NO_2$	−1.29	−0.92	−1.11	0.9
p-$Me_3SiC_6H_4NO_2$	−1.26	−0.84	−1.05	1.0

a) Scan rate: 80 mV/s.

It is seen that from the values of the ratio of i_{pa} to i_{pc} all the compounds are chemically stable during the electron transfer over a wide range of scan rates. However, the features of the potentials for ***para*** silyl and tolyl compounds are distinctly different from those of ***ortho*** and ***meta*** compounds. Thus, the value of $|E_{pc}|-|E_{pa}|$ of the former is about one-half relative to the latter two. It could be interpreted in terms of the poor reversible electron-transfer process in the ***ortho*** and ***meta*** compounds, the peak separation of which increased at a higher scan rate. The E_{pc} values for the compounds became more cathodic by 400 mV on 10-fold increase in the scan rate (40 mV/s→400 mV/s). At 3 V/s scan the peak separation reached 1.6 V.

2,4-Dinitrophenyltrimethylsilane. Cyclic voltammograms of 2,4-dinitrophenyltrimethylsilane, 2,4-dinitrotoluene and *m*-dinitrobenzene are shown in Figs. 1a—c. Of the compounds tested in the range of 0—−2.0 V, two cathodic peaks (R_1 and R_2) and the corresponding two anodic peaks (O_1 and O_2) appeared. When scanning was clipped at −1.20 V, the CV charts show that all the anion radicals, formed by one electron transfer (R_1), are chemically stable. However, in the scan range of 0—−2.0 V, the CV behavior among these compounds

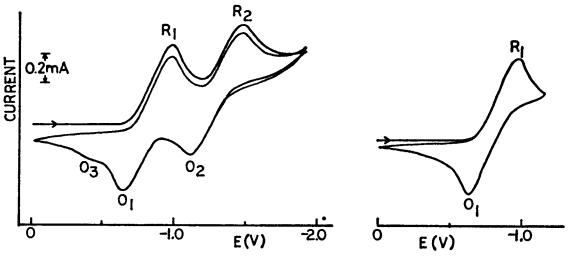

Fig. 1a. Cyclic voltammogram of 2,4-dinitrophenyltrimethylsilane. (First and second cyclic scan; scan rate: 80 mV/s.)

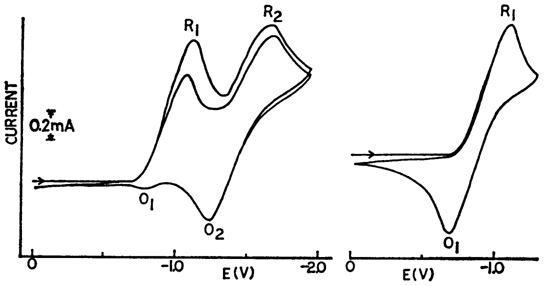

Fig. 1b. Cyclic voltammogram of 2,4-dinitrotoluene. (First and second cyclic scan; scan rate: 80 mV/s.)

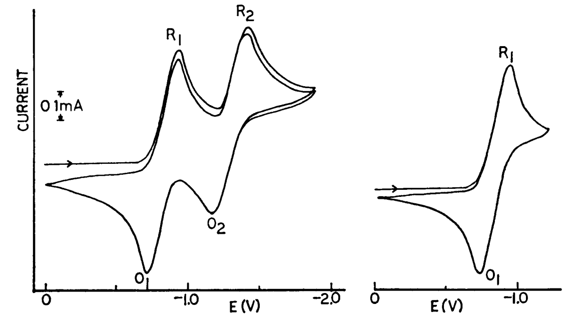

Fig. 1c. Cyclic voltammogram of *m*-dinitrobenzene. (First and second cyclic scan; scan rate: 80 mV/s.)

differed significantly. Thus, on potential reversal, 2,4-dinitrophenyltrimethylsilane exhibited a weak third anodic peak (O_3) at a low potential (Fig. 1a), which was absent when the potential was clipped at -1.20 V. This is presumably due to the reduction product which was derived from dianion. The explanation was supported by the fact that the addition of a proton donor such as methanol to the system causes an increase in peak O_3 and a decrease in peak O_1 and O_2, although the structure of the reduction product was not determined. On the other hand, the CV chart of 2,4-dinitrotoluene is very different from those of 2,4-dinitrophenyltrimethylsilane and *m*-dinitrobenzene. As Fig. 1b shows, the anodic peak of O_1 is extremely weak relative to the corresponding cathodic peak of R_1 when the scan was extended to -2.0 V. This fact indicates that the resulting anion radical is chemically unstable when it was allowed to stand until the second peak is swept and one electron removal from the anion radical to the starting compound is slow compared with chemical process.

The above observation might be expressed as following equations (1 and 2):

2,4-Dinitrophenyltrimethylsilane (DNS)

$$[\mathrm{DNS}] \xrightleftharpoons[-e(O_1)]{+e(R_1)} [\mathrm{DNS}]^{\overline{\cdot}} \xrightleftharpoons[-e(O_2)]{+e(R_2)} [\mathrm{DNS}]^{=} \quad (1)$$

2,4-Dinitrotoluene (DNT)

$$[\mathrm{DNT}] \xrightleftharpoons[-e(O_1)]{+e(R_1)} [\mathrm{DNT}]^{\overline{\cdot}} \xrightleftharpoons[-e(O_2)]{+e(R_2)} [\mathrm{DNT}]^{=} \quad (2)$$

From the values of peak separation of $|R|-|O|$ in Figs. 1a and 1b, that the silane compound has better reversibilities (Eq. 1) than the toluene in the electron transfer processes could be interpreted in terms of the substituent effect, in which the trimethylsilyl group contributes to stabilize the system *via* (p-d)π bonding between silicon and benzene ring, although the both dianions are considered to be highly reactive species. With respect to $[\mathrm{DNS}]^{\overline{\cdot}}$ and $[\mathrm{DNS}]^{=}$, many resonance structures are possible and the evidence for such a structure has been shown by ESR spectrum in the electrochemical reduction of *p*-nitrophenyltrimethylsilane.[7]

Experimental

Cyclic Voltammetry. All measurements were performed in purified anhydrous *N,N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte using a divided cell. The working electrode is a platinum inlay electrode (Beckman 32273) and the counter electrode is a platinum wire. A saturated calomel electrode was used as a reference which was connected to the cell using two salt bridges, saturated KCl solution and DMF–TBAP solution. A Hokuto Denko Model HB-107A function generator and Hokuto Denko Model HA-101 potentiostat were used. Cyclic voltammetry performed at the scan rate of 40—400 mV/s was recorded using a Rikadenki X-Y recorder Model BW 133. For higher speed recording, two channel wave memory, NF Model WM-812A, was employed. All runs were made after a 15 min purge with purified nitrogen and within 30 min of preparing the solutions.

Materials. Nitrophenyltrimethylsilanes and 2,4-dinitrophenyltrimethylsilanes were obtained by the method reported elsewhere.[8] Mono- and di-nitrotoluenes and *m*-dinitrobenzene were commercially available (extra pure grade).

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