PHYSICAL CHEMISTRY

S. G. MAIRANOVSKII, V. A. PONOMARENKO, N. V. BARASHKOVA

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

S. G. MAIRANOVSKII, V. A. PONOMARENKO, N. V. BARASHKOVA
and A. D. SNEGOVA

POLAROGRAPHIC STUDY OF IODOMETHYLTRIALKYLSILANES

AN UNUSUAL POLAROGRAPHIC MAXIMUM ON THE WAVE OF IODOMETHYLPHENYLDIMETHYLSILANE

(Presented by Academician A. A. Balandin, 29 IV 1960)

Up to the present time there have been no data in the literature on the polarographic behavior of organosilicon compounds. In the only published article (1) devoted to the polarography of chlorosilanes, the waves observed apparently pertain not to silanes, but to the discharge of the pyridinium ion formed during the hydrolysis of chlorosilanes in aqueous pyridine.

In the present work the polarographic behavior of organic molecules containing silicon was investigated for the first time. We studied the influence of the trialkylsilyl group on the electrochemical cleavage of the adjacent C—J bond. For this purpose the polarographic behavior was investigated of iodomethyltrimethylsilane (I), iodomethyldiethylmethylsilane (II), iodomethyl-di-*n*-propylmethylsilane (III), iodomethyl-di-*n*-butylmethylsilane (IV), and iodomethyldimethylphenylsilane (V). For comparison, polarograms were also recorded for primary *n*-butyl iodide (VI) and primary isobutyl iodide (VII).

The polarograms were recorded in 57 vol. % ethanolic solution at 25° in a thermostated cell of a design described previously (2). The dropping electrode had a paddle for forced detachment of drops; its characteristics were: $m = 1.52$ mg/sec, $t = 0.23$ sec, $m^{2/3}t^{1/6} = 1.032$ mg$^{2/3}\cdot$sec$^{-1/2}$. The anode was an external saturated calomel electrode. The curves were recorded on a recording polarograph of the Central Laboratory of Automation (3), with potentiometric control of the potentials relative to an auxiliary external aqueous saturated calomel electrode, as described earlier (4).

The silanes investigated in the work were prepared as follows. For the synthesis of compounds I—IV, a method developed earlier by one of us (5) was used, consisting in the interaction of chloromethylmethyldichlorosilane with alkylmagnesium iodides:

$$(CH_3)Cl_2SiCH_2Cl + 2RMgJ \rightarrow (CH_3)(R)_2SiCH_2Cl + 2MgClJ \rightarrow$$

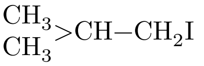
$$\rightarrow (CH_3)(R)_2SiCH_2J + MgCl_2 + MgClJ,$$

where $R = CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9$.

For the reactions, 0.25 mole of chloromethylmethyldichlorosilane and the corresponding amount of alkylmagnesium iodide in 150-200 ml of absolute ether were taken. After the addition of chloromethylmethyldichlorosilane to the Grignard reagent was completed, the ether was distilled off, and the residue was heated on a water bath at 80-85° for 15-16 hr. The distilled-off ether was added to the reaction products, the mixture was decomposed with water, the ether layer was dried over anhydrous Na_2SO_4, the ether was distilled off, and the products were fractionated on a column under vacuum. The yield of iodides in going from $(CH_3)_3SiCH_2J$ to $(C_4H_9)_2(CH_3)SiCH_2J$ decreased

···with 61 to 8%. In this connection, synthesis of V was carried out by reacting $(C_6H_5)(CH_3)_2SiCH_2Cl$ (13.2 g) with KI (17 g) in 170 ml of absolute acetone under reflux for 57 h. Yield of V: 43% of theory. Before polarograms were recorded, all iodides were again distilled under vacuum. The properties of the iodomethylsilanes obtained are presented in Table 1.

Table 1

No.	Substance	B.p., °C	n_D^{20}	d_4^{20}	$E_{1/2}$ rel. N.C.E.	Slope, mV^{-1}
I	$(CH_3)_3SiCH_2I$	140.5 (743.5)	1.4891	1.4301	−1.580	136
II	$(C_2H_5)_2(CH_3)SiCH_2I$	102.5 (50)	1.5000	1.3600	−1.603	140
III	$(C_3H_7)_2(CH_3)SiCH_2I$	82 (6)	1.4820	1.2694	−1.630	200
IV	$(C_4H_9)_2(CH_3)SiCH_2I$	89.5 (12)	1.4877	1.2116	−1.632	230
V	$(C_6H_5)(CH_3)_2SiCH_2I$	97.2 (3)	1.5730	1.4486	−1.470	150
VI	n-C_4H_9I	–	–	–	−1.782	100
VII	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH{-}CH_2I$	–	–	–	−1.795	95

At low concentrations, all the substances studied give distinct single-step reduction waves, whose limiting currents, as shown by experiments at different heights of the mercury column, are limited by diffusion of the depolarizer. The values of the diffusion-current constant $i_{\text{diff}}/Cm^{2/3}t^{1/6}$ for the substances studied range from 1.9 to 2.2 $\mu A/mM \cdot mg^{2/3} \cdot s^{-1/2}$. Calculation of the number of electrons participating in the electrode stage, according to the Ilkovič equation (assuming that the diffusion coefficient is of the order of $3 \cdot 10^{-6}$ cm^2/s), gave a value of 2. The half-wave potentials ($E_{1/2}$) of the substances studied do not depend on pH. Thus, the reduction of the compounds we investigated evidently proceeds by the same mechanism as

Fig. 1. Dependence of $E_{1/2}$ (circles), for V (A) and VII (B), and also of the ψ'-potential on the concentration of potassium chloride

the reduction of other haloalkyls—with the transfer of two electrons and replacement of the halogen of the organic molecule by hydrogen. The logarithmic plots of the waves of all the substances studied,

$$\lg \frac{i}{i_{\mathrm{lim}} - i} = f(E),$$

are rectilinear; the large values of the reciprocals of their slopes (Table 1) indicate the irreversible character of the waves. The values of $E_{1/2}$ of the waves, determined from the logarithmic plots, within experimental error do not depend on the concentration of the depolarizer.

In Table 1 the $E_{1/2}$ values of the waves of the substances studied are given for a 0.09 N concentration of potassium chloride. Comparison of the $E_{1/2}$ values for the compounds investigated shows that compounds I–IV, i.e., derivatives of alkylsilanes, have very similar $E_{1/2}$ values (see Table 1), whereas V, which contains a phenyl group at silicon, is reduced considerably more readily. Such behavior of the compounds studied is quite natural: the magnitude

alkyl radicals has almost no effect on the electronegativity of the trialkylsilyl residue and, consequently, almost does not influence the weakening of the adjacent C–I bond. The small shift of $E_{1/2}$ toward negative values with increasing alkyl radicals is apparently associated with a steric factor (^{6}). Introduction of phenyl into the silyl group increases its electronegativity and, moreover, increases its polarizability; therefore the nucleophilic cleavage of the C–I bond in V proceeds much more readily than in alkylsilyl derivatives.

Comparison of the $E_{1/2}$ values of iodoalkylsilanes and iodoalkanes (Table 1) shows that introduction of an alkylsilyl group into the iodoalkane molecule lowers the value of $E_{1/2}$, i.e., as it were facilitates nucleophilic cleavage of the C–I bond; thus the alkylsilyl group appears to be more electronegative than alkyls. This conclusion, however, does not agree with earlier observations (^{7}), according to which replacement of the hydrocarbon residue of carboxylic acids by the same group, but containing silicon in the α-position to the carboxyl, decreases the acid dissociation constant. Consequently, the alkylsilyl group has greater electron-donor properties than the corresponding hydrocarbon residue. The decrease in $E_{1/2}$ for reduction of the C–I bond on going from haloalkanes to silicon derivatives is apparently (^{8}) connected with a large difference in the adsorption and solvation energies of the starting substances and of the products formed at the electrode in the potential-determining stage between organosilicon and silicon-free compounds.

Fig. 2. Polarograms of V at different concentrations: 1 –0; 2 –$0.573 \cdot 10^{-3}$ M; 3 –$1.093 \cdot 10^{-3}$ M; 4 –$2.00 \cdot 10^{-3}$ M; 5 –$2.78 \cdot 10^{-3}$ M

Figure 1: Fig. 2. Polarograms of V at different concentrations: 1 –0; 2 –$0.573 \cdot 10^{-3}$ M; 3 –$1.093 \cdot 10^{-3}$ M; 4 –$2.00 \cdot 10^{-3}$ M; 5 –$2.78 \cdot 10^{-3}$ M

Fig. 3. Polarograms of V at $h_{\mathrm{Hg}} = 30$ cm (A) and 110 cm (B). 1 –$C_{\mathrm{V}} = 2.99$ mM in the absence of BCTEA, 2 –$C_{\mathrm{V}} = 2.64$ mM in the presence of 0.083 M BCTEA against a background of 0.09 N KCl in 57% ethanol

Figure 2: Fig. 3. Polarograms of V at $h_{\mathrm{Hg}} = 30$ cm (A) and 110 cm (B). 1 –$C_{\mathrm{V}} = 2.99$ mM in the absence of BCTEA, 2 –$C_{\mathrm{V}} = 2.64$ mM in the presence of 0.083 M BCTEA against a background of 0.09 N KCl in 57% ethanol

Fig. 2. Polarograms of V at different concentrations: 1 –0; 2 –$0.573 \cdot 10^{-3}$ M; 3 –$1.093 \cdot 10^{-3}$ M; 4 –$2.00 \cdot 10^{-3}$ M; 5 –$2.78 \cdot 10^{-3}$ M

Fig. 3. Polarograms of V at $h_{\mathrm{Hg}} = 30$ cm (A) and 110 cm (B). 1 –$C_{\mathrm{V}} = 2.99$ mM in the absence of BCTEA, 2 –$C_{\mathrm{V}} = 2.64$ mM in the presence of 0.083 M BCTEA against a background of 0.09 N KCl in 57% ethanol

A noticeable influence on the $E_{1/2}$ of the waves of the compounds studied is exerted by the nature and concentration of the indifferent electrolyte. As already noted, the waves are irreversible in character and, according to the theory of slow discharge of A. N. Frumkin (^{9}), the influence of the indifferent electrolyte on $E_{1/2}$ should be determined mainly by a change in the ψ'-potential.

In Fig. 1, points *A* and *B* show the experimental values of $E_{1/2}$ for waves V and VII in 57% alcohol solutions with different concentrations of KCl. The curves in the same figures show the change in the ψ'-potential, calculated according to Stern (^{10}); for the calculations the dielectric constant was taken as 50, and the double-layer capacitance as 16 and 18 μF/cm^2 for Fig. 1 *A* and *B*, respectively. From Fig. 1 it is evident that the shift of $E_{1/2}$ with increasing potassium chloride concentration is indeed associated with a decrease in the ψ'-potential. As was to be expected, a considerably larger shift of $E_{1/2}$ in the anodic direction is observed upon addition of surface-active cations to the solution. Thus, when tetraethylammonium benzenesulfonate (BTEA) is introduced into a 0.1 *N* KCl solution, up to a concentration of the latter of 0.08 *N*, $E_{1/2}$ of V shifts toward positive potentials by ~ 110 mV. A small shift of $E_{1/2}$ of V in the anodic direction is also observed upon addition of gelatin to the solution.

Because of the irreversibility of the electrode process, the values of $E_{1/2}$ depend on the height of the mercury column h_{Hg}. Thus, when h_{Hg} is doubled, $E_{1/2}$ of I becomes ~ 25 mV more negative, which agrees well with the conclusions of the theory (^{11}).

Fig. 4. Dependence of the heights of the apparent steps on wave V on the height of the mercury column. 1 –upper step, 2 –lower step, 3 –total (diffusion)

Fig. 4

Figure 3: Fig. 4

current. $C_\mathrm{V} = 2.64$ mM

Very interesting phenomena are observed on the waves of V —iodomethylphenyldimethylsilane. When the concentration of V in solution is raised above ~ 1.0 mM, a small maximum appears in the middle portion of the wave, giving the impression that the wave is divided into two steps (Fig. 2). Upon addition of BTEA to the solution, the curves shift toward positive potentials and the maximum on them moves to its "usual position" —to the upper part of the wave (Fig. 3). Interestingly, the potential of the maximum remains almost unchanged. With increasing height of the mercury column, the maximum on wave V in the presence of BTEA decreases; in exactly the same way it also decreases in solution without BTEA, the division of the wave into two apparent steps becoming less pronounced. Figure 3 shows polarograms of V at two h_Hg values (30 cm (A), 110 cm (B)) in the absence of BTEA (1) and in its presence (2). Figure 4 gives the dependence of the heights of the apparent steps of wave V on h_Hg.

Addition of gelatin to the solution (up to 0.05%) completely eliminates the maximum on wave V; wave V thereby becomes more drawn out.

Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
28 IV 1960

REFERENCES

1. E. A. Abrahamson, C. A. Reynolds, *Anal. Chem.*, **24**, 1827 (1952).
2. S. G. Mairanovskii, F. S. Titov, *ZhAKh*, **15**, 121 (1960).
3. S. B. Tsfasman, *Zav. lab.*, **22**, 131 (1956).
4. S. G. Mairanovskii, A. A. Fainzil' berg et al., *DAN*, **125**, No. 2, 351 (1959).
5. V. A. Ponomarenko, V. F. Mironov, *DAN*, **94**, No. 3, 485 (1954).
6. F. L. Lambert, K. Kobayashi, *Chem. and Ind.*, **30**, 949 (1958).
7. P. D. George, M. Prober, J. R. Elliott, *Chem. Rev.*, **56**, 1161 (1956).
8. N. S. Hush, *Zs. Elektrochem.*, **61**, 734 (1957).

9. A. N. Frumkin, V. S. Bagotskii et al., *Kinetics of Electrode Processes*, M., 1952, p. 177.

10. Ibid., p. 15.

11. P. Delahay, *New Instruments and Methods in Electrochemistry*, IL, 1957, p. 103.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.