STRUCTURE AND POLAROGRAPHIC BEHAVIOR OF CERTAIN IODOMETHYLTRIALKYL(ARYL)SILANES

(UDC 543.253)

S. G. Mairanovskii, V. A. Ponomarenko,
N. V. Barashkova, and M. A. Kadina

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11,
pp. 1951-1956, November, 1964
Original article submitted January 31, 1963

In our first report [1] we established the mechanism of the reduction of iodomethyltriarylsilanes on a dropping mercury electrode and showed that in a number of cases the appearance of unusual maxima is observed on the waves. Continuing and deepening our polarographic investigations of iodomethyltrialkylsilanes, we found that some of them give two-step waves on the polarograms; this might mean that comparatively stable free radicals, the reduction of which takes place at more negative potentials than the initial molecules, arise at the first stages of the reduction process. The detection of this phenomenon prompted us to investigate in greater detail the nature of the doubling of the waves of certain iodomethylalkylsilanes, as well as to synthesize and investigate a number of new compounds, to trace the influence of the structure of the iodomethylsilane derivatives on the polarographic half-wave potentials of both steps. The results of these investigations are presented in this work.

EXPERIMENTAL

The polarograms were taken on the PÉ-312 recording instrument against a background of a 0.09 N solution of KCl in 57% alcohol. The potentials on the polarograms were monitored potentiometrically with a supplementary removable saturated calomel electrode [2]. The dropping electrode with forced breakoff of the drops, according to Skobets and Kavetskii [3], possessed the characteristics m = 1.07 mg/sec, t = 0.26 sec. Certain experiments were conducted on a special electrode with a movable spatula, permitting a change in the period of dropping t with practically unchanged mass of the effluent mercury m = 0.8 mg/sec. All the experiments were conducted in a thermostatically controlled cell [4] at a temperature of 25 ± 0.2 deg (except for special experiments studying the influence of temperature on $E_{\frac{1}{2}}$ of each of the steps).

The compounds used in the work were obtained according to the schemes

$$\text{A.}\ \mathrm{ClCH_2Si(CH_3)_2Cl + RMgBr \xrightarrow[\text{ether}]{\text{abs.}} ClCH_2Si(CH_3)_2R + MgBrCl}$$

compounds (I) — (V)

$$\text{B.}\ \mathrm{RSi(CH_3)_2CH_2Cl + KI \xrightarrow[\text{(boiling 77 h)}]{\text{abs. acetone}}}$$

$$\mathrm{\rightarrow RSi(CH_3)CH_2I + KCl}$$

compounds (VI) — (X)

The yields, elementary analysis, physical properties, and values of the half-wave potentials for the first and second steps are presented in Tables 1 and 2 for the investigated compounds.

DISCUSSION OF EXPERIMENTAL RESULTS

The greatest difference in the potentials of the first and second steps on the polarographic waves is observed in the case of iodomethyltriethylsilane (I); hence, a study of the influence of various factors on the separation of the steps was conducted for the example of the waves of (I) to establish the nature of the doubling of the wave. Just as in the case of other derivatives of iodomethyltrialkylsilanes, on the polarograms of (I) at concentrations above about

TABLE 1. Properties of Investigated Iodomethyltrialkyl(aryl)silanes and the Starting Materials

No.	Formula	B.p., °C, p, mm Hg	n_D^{20}	d_4^{20}	MR found	MR calc.	$E'_{1/2}$, V	$E''_{1/2}$, V	x_{SiR_3}
I	$(C_2H_5)_3SiCH_2Cl$	48—50 (10)	1,4472						
II	$CF_3CH_2CH_2Si(CH_3)_2CH_2Cl$*	56,3(2)	1,4342	1,0461	45,0	44,38	—	—	—
III	p-$FC_6H_4Si(CH_3)_2CH_2Cl$*	74—76(2)	1,5042	1,0990	55,01	55,10	—	—	—
IV	p-$ClC_6H_4Si(CH_3)_2CH_2Cl$*	116(4)	1,5370	1,1385	59,82	59,96	—	—	—
V	m-$CF_3C_6H_4Si(CH_3)_2CH_2Cl$*	72(2)	1,4701	1,1778	58,68	59,0	—	—	—
VI	$(C_2H_5)_3SiCH_2I$	216—217	1,5036	1,3418	56,50	57,03	—1,54	—1,72	2,076
VII	$CF_3CH_2CH_2SiCH_2I(CH_3)_2$*	89—90(3)	1,4900	1,5080	53,0	52,4	—1,33	—1,54	2,102
VIII	p-$FC_6H_4Si(CH_3)_2CH_2I$*	105,5(3)	1,5558	1,4970	63,0	63,03	—1,40	—1,53	2,101
IX	p-$ClC_6H_4Si(CH_3)_2CH_2I$ *	136(4)	1,5851	1,5237	67,98	67,84	—1,37	—1,50	2,080
X	m-$CF_3C_6H_4Si(CH_3)_2CH_2I$*	96—97(3)	1,5160	1,5349	66,80	66,46	—1,34	—1,45	2,102
XI	$(C_2H_5)_2Si(CH_3)CH_2I$	102,5(50)	1,5000	1,3690	52,02	52,40	—1,56	—1,70	2,082
XII	$(n$-$C_3H_7)_2Si(CH_3)CH_2I$	82(6)	1,4920	1,2694	52,79	53,64	—1,60	—1,76	2,084
XIII	$(n$-$C_4H_9)_2Si(CH_3)CH_2I$	99,5(12)	1,4877	1,2116	61,35	62,90	—1,58	—1,79	2,084
XIV	$C_6H_5Si(CH_3)_2CH_2I$	97,2(3)	1,5730	1,4436	62,77	62,81	—1,43	—1,56	2,097

---

*Compounds produced for the first time.

TABLE 2. Yield and Analysis of Investigated Iodomethyltrialkyl(aryl)silanes

No.	Synthesis method	Yield, %	Found, %					Calculated, %				
			C	H	Cl	F	I	C	H	Cl	F	I
I	A	49,7	50,12	10,42	21,63	—	—	50,08	10,35	21,55	—	—
II	A	21	35,15	5,9	17,35	28,3	—	35,35	5,70	17,20	28,0	—
III	A	52,0	53,32	5,82	17,7	9,62	—	53,2	5,90	17,50	9,7	—
IV	A	30,0	49,62	5,2	32,6	—	—	49,50	5,5	32,2	—	—
V	A	33,0	47,29	5,09	14,23	22,2	—	47,5	4,75	14,10	22,5	—
VI	B	25,5	—	—	—	—	—	32,80	6,63	—	—	—
VII	B	27,5	24,27	4,56	—	19,33	43,2	24,20	4,40	—	19,15	42,9
VIII	B	62	36,81	4,58	—	6,32	43,5	36,65	4,75	—	6,3	43,15
IX	B	52	34,52	3,77	11,42	—	40,32	34,45	3,85	11,35	—	40,50
X	B	21	34,78	3,57	—	16,50	37,20	34,95	3,45	—	16,60	37,00

1.0 mM, the appearance of a maximum is observed, distorting the shape of the wave. To obtain undistorted waves, we worked with comparatively low concentrations of the silanes: from 0.05 to 0.5 mM. The cause of the difference in the diffusion-limited wave may be either a step-wise occurrence of the electrochemical reaction or an accelerating influence of the adsorption of the starting material [5], or an inhibiting action [6,7] of the strongly adsorbed reaction product. The heights of the individual steps on the polarograms of (I) are equal, and this equality of the heights of the steps is preserved both when the temperature is raised from 25 to 55°, and when the dropping period of the electrode t is varied from 0.25 to 5 sec. Both steps possess a diffusion character. Consequently, the two-step character of the wave on the polarograms of (I) is related not to adsorption effects, but is due to a two-step reduction of iodomethyltriethylsilane. The mechanism of its reduction on a dropping mercury electrode, considering the fact that the height of the summary wave corresponds to the transition of two electrons [1], can be represented by the following scheme:

$$R_3SiCH_2I + e^- \rightarrow R_3SiCH_2^{\cdot} + I^- \qquad (1)$$

$$R_3SiCH_2^{\cdot} + e^- \rightarrow R_3SiCH_2^- \qquad (2)$$

$$R_3SiCH_2^- + H_2O \rightarrow R_3SiCH_3 + OH^- \qquad (3)$$

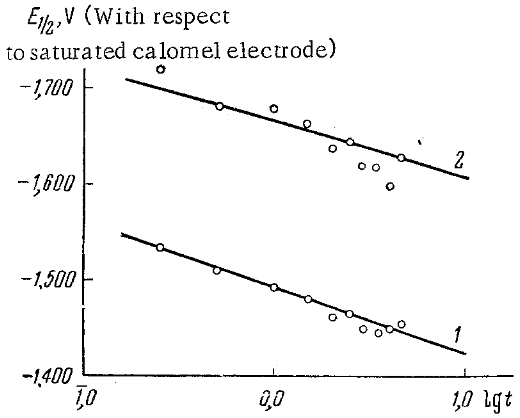

Fig. 1. Dependence of $E_{\frac{1}{2}}$ of the first (1) and the second (2) waves on the polarograms of iodomethyltriethylsilane on the logarithm of the dropping period of the dropping electrode. m = const = 0.80 mg /sec.

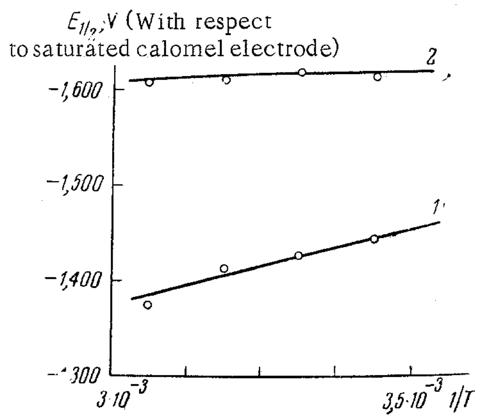

Fig. 2. Dependence of $E_{\frac{1}{2}}$ of the first (1) and the second (2) waves on polarograms of (I) on the reciprocal of the temperature. The potentials were measured with respect to a saturated calomel electrode at 25°.

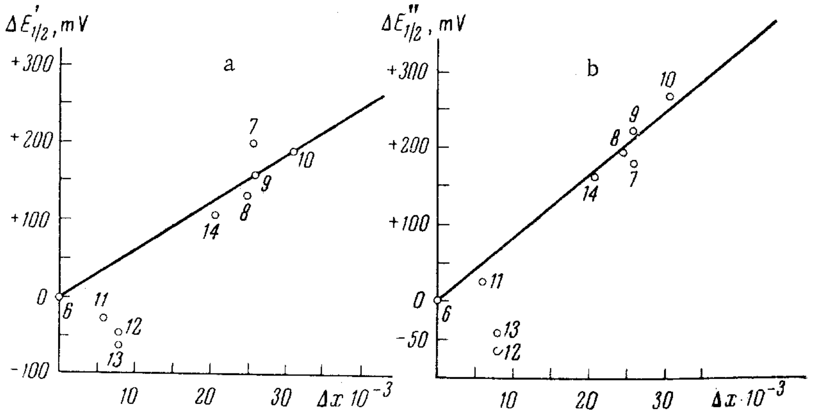

Fig. 3. Relationship of the first (a) and second (b) half-wave potentials of the reduction of iodomethyltrialkyl(aryl)silanes with the polarity constants of the silyl groups. The numbers of the points correspond to the notations of the compounds cited in Table 1.

where process (1) corresponds to the first wave on the polarograms, process (2) to the second. The half-wave potentials ($E_{\frac{1}{2}}$) of both stages do not depend on the pH of the solution; consequently, the hydrogen ions do not participate in the potential-determining steps. Graphs of the waves in a plot of $\log[i/(i_{\lim} - i)]$ versus E are linear; the reciprocals of the slopes of the graphs for the first wave of (I), about 130 mV, and the second, about 100 mV, give evidence of irreversibility of the transfer of electrons in both stages of the reduction.

The difference in the values of the slope of the logarithmic curves of waves 1 and 2, i.e., the transport coefficients α, can be used for a still greater separation of the waves on the polarograms. According to the theory of irreversible processes, $E_{\frac{1}{2}}$ is related to t by the function [8]

$$E_{1/2} = \text{const} + \frac{RT}{2\alpha n_a F} \ln t \tag{4}$$

where R, T, and F are the gas constant, absolute temperature, and Faraday's number, respectively; n_a is the number of electrons transferred in the potential-determining step (in this case, for both steps $n_a = 1$).

The value of the coefficient in front of the logarithm is none other than half the reciprocal of the slope of the logarithmic curve of the corresponding wave; hence, as can be seen from Eq. (4), as t increases, $E_{\frac{1}{2}}$ of the first wave should be displaced more toward positive potentials than $E_{\frac{1}{2}}$ of the second wave, and thus, as t increases, the two waves on the polarograms of (I) should move apart. Figure 1 presents the dependence of $E_{\frac{1}{2}}$ of both steps on log T, obtained from experiments with an electrode possessing a movable spatula. The points in Fig. 1 correspond to the experimental values, while the straight lines were constructed according to Eq. (4). The experimental values are arranged close to the theoretical straight lines. Noteworthy is the large dispersion of values of $E_{\frac{1}{2}}$ around the theoretical values. This is due to the comparatively low accuracy of the determinations of E and their relatively poor reproducibility (±10-15 mV) for the waves of (I) and certain other iodomethyltrialkylsilanes. The basic cause of the poor reproducibility evidently lies in the influence of solutions of the substances studied on the working system of the dropping electrode; for example, during the process of taking of the polarograms, irregular variations of the dropping period are periodically observed.

When the temperature is increased, the waves on the polarograms of (I) distinctly diverge. This is due to the substantial positive temperature coefficient of $E_{\frac{1}{2}}$ of the first wave, and the practically temperature-invariant value of $E_{\frac{1}{2}}$ of the second wave (see Fig. 2).

The presence of two steps on the polarograms of certain iodomethyltrialkylsilanes prompted us to compare $E_{1/2}$ individually for the first and second waves with the structure of the discharging particles. The values of $E_{1/2}$ of the waves of the compounds investigated in this work, as well as the converted values for two-step waves $E_{1/2}$ of certain substances studied earlier [1 , are cited in Table 1. In those cases when the steps diverge poorly on the polarogram, values of $E_{1/4}$ and $E_{3/4}$ of the total (summary) wave were taken as $E_{1/2}$ of the first and second steps. The presence of two steps on the polarograms of the compounds was judged according to the point of inflection on the graphs of the waves as a plot of log $\frac{i}{(i_{lim} - i)}$ versus E, the summary limiting current of the investigated wave being taken as i_{lim}.

From a consideration of the data of Table 1, it follows that $E_{\frac{1}{2}}$ both of the first and of the second steps are displaced toward more negative potentials with increasing electronegativity of substituents at the silicon atom. We attempted to follow this dependence quantitatively, comparing the values of $E_{\frac{1}{2}}$ with the polarity constants (X_{SiR_3}) of the silyl groups. The values of X_{SiR_3} for all the indicated groups were determined according to the method that we described earlier [9]. The values of X_{SiR_3} are related to the sum of the Taft polarity constants for the R groups next to the silicon by an approximate linear function [10]. They can be used in a number of cases for a quantitative estimation of the reactivity of organosilicon compounds

$$\lg k / k_0 = c(X - X_0)$$

$$\Delta E_{1/2} = (E_{1/2}) - (E_{1/2})_0 = c\,(X - X_0)$$

The results of a comparison of the quantities $X - X_0$ and $\Delta E_{\frac{1}{2}}$ for the first and second half-wave potentials are cited in Figs. 3a and 3b. $(C_2H_5)_3SiCH_2I$ was used as the standard for the comparison of $(E_{\frac{1}{2}})_0$ and X_0. As can be seen from Fig. 3b, the correlation of ΔX and $\Delta E_{\frac{1}{2}}$ for the second wave is rather good within the limits of the experimental error, with the exception of the compounds $(C_3H_7)_2(CH_3)SiCH_2I$ and $(C_4H_9)_2(CH_3)SiCH_2I$. Far poorer correlation is observed for the first wave (see Fig. 3a). The dropout of the points for $(C_3H_7)_2(CH_3)SiCH_2I$ and $(C_4H_9)_2(CH_3)SiCH_2I$ in both cases is evidently due to steric factors. The accumulation of large-sized substituents at the silicon leads to an inhibition of the electrode process, which agrees with the data that we obtained earlier [1].

SUMMARY

1. The observed doubling of the two-electron polarographic reduction waves of iodomethyltrialkyl(aryl)silanes into two one-electron waves is due to the formation of comparatively stable radicals: intermediate products of the reduction process.

2. It was shown for the example of iodomethyltriethylsilane that the individual steps move apart along the potential axis as the dropping period and temperature increase.

3. The values of the half-wave potentials of both stages of the reduction of the indicated iodides are correlated for most compounds with the values of the polar constants of the silyl groups.

LITERATURE CITED

1. S. G. Mairanovskii, V. A. Ponomarenko, N. V. Barashkova, and A. D. Snegova, DAN SSSR, 134, 387 (1960).
2. S. G. Mairanovskii, A. A. Fainzil'berg, S. S. Novikov, and V. A. Klimova, DAN SSSR, 125, 351 (1959).
3. E. M. Skobets and N. S. Kavetskii, Zavod. laboratoriya, 15, 1299 (1949).
4. S. G. Mairanovskii, and F. S. Titov, Zh. Analit. Khimii, 15, 121 (1960).
5. A. B. Érshler, G. A. Tedoradze, and S. G. Mairanovskii, DAN SSSR, 145, 1324 (1962).
6. M. A. Loshkarev and A. A. Kryukova, ZhFKh, 30, 2236 (1956).
7. B. Kastening and L. Holleck, Z. Elektrochem., 63, 116 (1959).
8. P. Delahey, New Instruments and Methods in Electrochemistry [Russian translation] (IL, Moscow, 1957), p. 103.
9. V. A. Ponomarenko, E. M. Zakharov, N. A. Zadorozhnyi, and A. D. Petrov, DAN SSSR, 132, 619 (1960).
10. L. A. Leites, Yu. P. Egorov, G. Ya. Zueva, and V. A Ponomarenko, Izv. AN SSSR, Otd. Khim. N., 1961, 2131.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
