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A NEW METHOD FOR THE DETERMINATION OF WATER IN ORGANIC SOLVENTS, AND SOME COMMENTS ON AN ELECTROCHEMICAL METHOD OF SYNTHESIZING Si—Si BONDS

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Summary

The features of the electrochemical reduction of halogenosilanes are investigated, taking into account previous reports. The high sensitivity of chlorosilanes to hydrolysis is pointed out as a possible source of misleading reduction waves. This side reaction can also be applied to the water contents in organic solvents with a precision in the range to that obtained with the Karl Fischer method.

Introduction

The paper by Hengge and Firgo entitled "An electrochemical method for the synthesis of silicon—silicon bonds" [1] prompt us to report results on the analytical titration of water in organic solvents by polarography, using chlorosilanes as titrating agents.

As we mentioned in our papers [2], apparently overlooked by Hengge and Firgo, under the experimental conditions used for polarography, the hydrolysis of the halogenosilanes by residual water in the solvents is very fast. Polarographic measurements were carried out with halogenosilanes in 1—6 × 10^{-3} M concentration range and the water concentration, even with very carefully "dried" solvents cannot be lower than that. For example in 1—2 dimethoxyethane (DME) after distillation over $AlLiH_4$, the water content was 0.03% (18 × 10^{-3} M). Since the hydrolysis is very fast, the halogenosilanes are completely hydrolysed. Indeed, this well known reaction was suggested some years ago by Rochow [4] as a method of drying organic solvents.

Before describing the analytical determination of the water concentration in various solvents, we consider carefully the features of the electrochemical reduction of halogenosilanes.

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Results and discussion

I. Electrochemical reduction of Ph_3SiCl

For this compound Hengge and Firgo reported two polarographic waves in a 0.1 *M* TBAP *, DME solution: the first at —1.2 V and the second at —3.1 V vs. 0.001 *M* $AgClO_4$ (0.1 *M* TBAP)/Ag reference electrode. These values correspond to —0.5 V and —2.4 V vs. SCE **. The first wave was attributed to the formation of a radical and the second to the formation of an anion:

$$Ph_3SiCl + e^- \xrightarrow{-1.2\text{ V}} [Ph_3SiCl]^{\cdot -} \rightarrow [Ph_3Si]^{\cdot} + Cl^- \qquad (1)$$

$$Ph_3SiCl + 2\,e^- \xrightarrow{-3.1\text{ V}} Ph_3Si^- + Cl^- \qquad (2)$$

In our hands [2c], the polarogram of a pure sample in 0.1 *M* TBAP, DME solution, showed only a single wave, at —1.95 V vs. TBAI (sat), AgI/Ag reference electrode, i.e. at —2.45 V vs. SCE, corresponding to the second wave observed by Hengge [1], which he attributed to the anion formation. But this wave does not change when a large amount of phenol is added, which is inconsistent with the formation of an anion as in eq. 2. Moreover, coulometric data showed that only one electron is exchanged at this potential.

Furthermore exhaustive controlled potential electrolysis with a mercury pool cathode and platinum anode at —2.6 V vs. SCE (i.e. —2.2 V vs. AgI/Ag) led to a large amount of disiloxane (more than 50% yield), and 42% of $Ph_3SiSiPh_3$ was isolated [2c] rather than the 13.9% observed by Hengge, who worked without potential control, with a mercury pool anode and platinum cathode.

The polarograms changed with time (Fig. 1), and a second wave appeared at —1.4 V (vs. SCE) and increased with time; this wave corresponds to electroreduction of HCl.

II. Electrochemical reduction of Me_3SiCl

Hengge and Firgo observed one reduction wave at —2.2 V vs. $AgClO_4$/Ag reference electrode (i.e. at —1.5 V vs. SCE). We also observed only one wave at ~—1.4 V vs. SCE and assigned this to electroreduction of HCl [2b]. Linear sweep voltammetry curves for Me_3SiCl and HCl are identical (Fig. 2). They correspond to a reversible process, rather than an irreversible process as observed for reduction of halogeno-silanes and -germanes [2b,3]. Furthermore, exhaustive controlled potential electrolysis with a mercury pool cathode (at —1.5 V vs. SCE) gives only traces (less than 0.5%) of $Me_3SiSiMe_3$, which could be detected only by GLC. Gas evolution was observed corresponding to the HCl reduction. During electrolysis of Ph_3SiCl at —2.6 V vs. SCE, the similar gas evolution occurred before precipitation of $Ph_3SiSiPh_3$.

The mechanism of electrochemical reduction of halogenosilanes and germanes has been set out in detail [2c].

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[*] TBAP = Tetrabutylammonium perchlorate.

[**] SCE = Saturated calomel electrode.

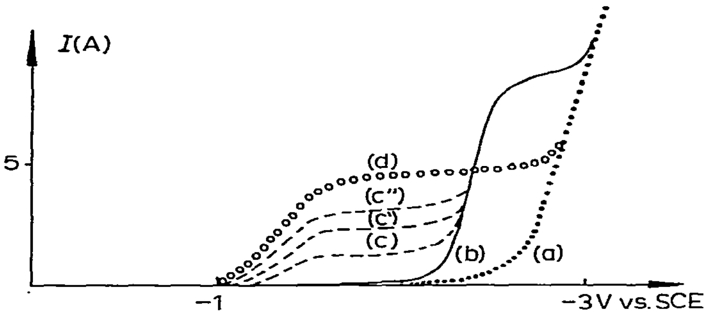

Fig. 1. Polarograms of (a) 0.1 *M* TBAP, DME solution; (b) with 7 m*M* Ph_3SiCl; (c) after 30 min; (c′) after 60 min; (c″) after 90 min; (d) as (a) with Me_3SiCl.

III. Water titration

The water content of organic solvents is generally measured by Karl Fischer's method as improved by Bizot [5]. On the basis of our polarographic results we propose another method. No electrochemical reduction of water occurs on mercury cathode when tetrabutylammonium salt is used and so it cannot be titrated directly. However, the water will hydrolyse chlorosilanes giving hydrochloric acid, and this reaction is quantitative when a nucleophilic catalyst (HMPA) is present [2a]. Thus, solvent dried by use of an excess of Ph_3SiCl in the presence of HMPA was used as a blank. Addition of solvent containing water causes an increase in the HCl concentration, and the diffusion current corresponding to the polarographic wave of HCl also increases, and this increase is directly related to the water concentration, so that the latter can be deduced from a standardization curve.

For this method, anisole was chosen as polarographic solvent, first because its residual water concentration is very low (<5 m*M*) and second because the 0.2 *M* TBAP, anisole solution has a sufficient conductivity to be used as polarographic solvent [6]. The standardisation curve obtained by plotting diffusion currents against known hydrochloric acid concentrations in anisole is a straight line.

Results of determinations carried out in this way are presented in Table 1; they are in good agreement with the values obtained by the Karl Fischer method.

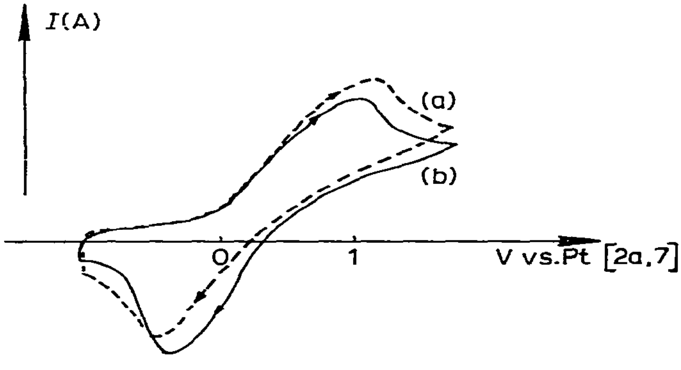

Fig. 2. Linear sweep voltammetry curves of (a) Me_3SiCl; (b) HCl in 0.1 *M* TBAP, DME solution.

TABLE 1

COMPARISON OF THE RESULTS FROM THE KARL FISCHER AND POLAROGRAPHIC METHODS

Solvent	Water concentration (mg l^{-1})	
	by Karl Fischer method	by polarographic method
Pentane	0 ± 10	0 ± 10
Cyclohexane	0 ± 10	0 ± 10
Light petroleum	20 ± 10	10 ± 10
Hexane	30 ± 10	40 ± 10
Anisole (dry)	100 ± 10	100 ± 10
Benzene	210 ± 20	180 ± 20
DME (commercial)	1200 ± 100	1600 ± 300
DME (dry)	250 ± 30	300 ± 30
Dioxane	300 ± 30	350 ± 30
Propylene carbonate	290 ± 30	300 ± 30
Ether	400 ± 40	420 ± 40
THF (dry)	1000 ± 50	950 ± 100
Methanol	2200 ± 100	2600 ± 200
Acetamide	3500 ± 100	3900 ± 300
Methylcyclohexanol	15000 ± 500	13000 ± 1000
Cyclohexanol	20000 ± 500	18000 ± 1000
Acetone	[a]	1200 ± 100

[a] Water concentrations in acetone cannot be measured by the Karl Fischer method since the Karl Fischer solution reacts with this solvent.

IV. Conclusion

From the results it is clear that the $[R_3Si]^{\cdot}$ radical cannot be formed reversibly at low cathodic potentials. Electroreduction of halogeno-silanes and -germanes take place irreversibly at higher cathodic potentials (< -2 V vs. SCE). At the lower potential (-1.4 V vs. SCE) the polarographic wave corresponds to the electroreduction of HCl formed by hydrolysis of the chlorosilanes. This hydrolysis is readily brought about, even by the traces of water contained in solvents, which gives rise to a new method for the determination of the water concentration.

Experimental

The polarogram of 20 ml of a solution of 0.2 *M* TBAP and 6×10^{-3} *M* Ph_3SiCl in anisole showed only one reduction wave, at -2.45 V vs. SCE. Addition of 5 μl of HMPA caused complete hydrolysis within three minutes, and the new polarogram, regarded as the blank, showed two waves at -1.4 V and -2.45 V vs. SCE. A known volume of the solvent was added by a syringe and the diffusion current at -1.4 V increased. This increase was plotted on the standardization curve. The corresponding hydrochloric acid concentration, equal to the water concentration, can be read off from the x axis. (The presence of a slight excess of Ph_3SiCl must be confirmed after measurement to ensure that all the water has reacted.)

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