Ultrasounds in voltammetry of irreversible processes of silicon organic compounds

In search of thermodynamic consequences†

Viatcheslav Jouikov,* Claude Bernard and Chantal Degrand

SEESIB Equipe Electroanalyse et Electrosynthèse Organique, (CNRS UMR 6504), Université Blaise Pascal, 63177 Aubière cédex, France

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The electron transfer in the course of the electrochemical oxidation of hexamethyldisilane and the electroreduction of chlorotrimethylsilane in anhydrous acetonitrile was shown to follow a dissociative mechanism. The same processes carried out upon sonication with ultrasounds of low (20 kHz) and high (500 kHz) frequency did not reveal any decrease of the effective potential. The effect of ultrasounds was only to intensify the mass transfer and to accelerate the Cl–F exchange of chlorotrimethylsilane with the fluorine anion provided by the supporting electrolyte.

Les ultrasons en voltamétrie des processus irréversibles des composés organique du silicium. A la recherche de conséquences thermodynamique. Il a été démontré que les réactions électrochimiques d'oxydation de l'hexaméthyldisilane et de réduction du chlorotriméthylsilane dans l'acétonitrile anhydre avaient lieu suivant un mécanisme de transfert d'électron dissociatif. Lorsque ces mêmes réactions sont conduites en présence d'ultrasons de basse ou de haute fréquence (20 ou 500kHz), aucune diminution du potentiel effectif n'est observé. L'unique effet des ultrasons a été d'accroître le transfert de masse et d'accélérer l'échange Cl–F du chlorotriméthylsilane avec l'anion fluorure de l'électrolyte support.

The influence of ultrasounds on electrochemical processes and, above all, on the mass-transfer intensification has been studied in a series of papers.[1–5] The lowering the potential of the irreversible oxidation of aromatic disulfides under the action of ultrasounds[6] has also been reported. Since the ultrasounds do not affect characteristics of stepwise processes,[7–9] one can suppose that it acts by disturbing the diffusion layer or by depassivating the electrode surface of adsorbed particles. Besides accelerating mass transfer and clearing the electrode surface, one can suppose another possible action of ultrasounds on voltammetric characteristics of irreversible processes. Sonication of an electrolyte can affect the double layer structure and, hence, the effective potential at the reaction site, so this potential might oscillate with the applied frequency. Higher harmonics of ultrasounds with a main frequency of several hundreds of kHz might overlap with the beginning of a zone of non-linearity in dielectric properties (ε_s) with frequency of common organic solvents. As a result, the solvent reorganization energy might change, resulting in a variation in the electron transfer activation barrier.

On the other hand, the electrosynthesis of silicon organic compounds is a very promising field of chemistry and an eventual possibility to modify the reaction mechanism by ultrasounds could be a good way to expand the synthetic potentialities of this method.

The purpose of this work was to determine the nature of the electron transfer in electrochemical oxidation and reduction of some silicon-containing compounds and to clarify possible consequences of the action of ultrasounds on electrochemically irreversible processes.

Results and discussion

Electrooxidation of hexamethyldisilane

Upon oxidation at a stationary Pt oxidized electrode, hexamethyldisilane shows an oxidation peak ($E_p = 1.667$ V *vs.* SCE) whose current is linear with concentration and with the square root of the potential sweep rate. The ratio $i_p \nu^{-1/2}$ remains constant within the sweep rate interval 0.05–1000 V s^{-1}. This indicates that the process is diffusion-controlled under the given experimental conditions. Peak width (at $\nu = 1$ V s^{-1}) corresponds to the transfer coefficient $\alpha = 0.38$. The number of electrons involved in oxidation was shown to be 2 per molecule. The slope of the dependence of E_p on the sweep rate $[\Delta E_p/\Delta \log(\nu)]$ is 76 mV (Fig. 1).

In the process of cation elimination, the Me_3Si^+ cation is a better leaving group than the proton.[10] For this reason the former does not exist in its free form in solution.[11] This particle is immediately intercepted by a nucleophile (*e.g.*, the anion of the supporting salt in the double or reaction layer) at the stage of charge induction in the transition state. Being nucleophile-assisted, electron transfer is therefore dissociative. The dissociative character of the process can also be deduced from the following consideration. Three main parameters, which determine the reactivity of the disilane upon oxidation [energy of the highest occupied molecular orbital, $\varepsilon_{HOMO} \sim E^0_{(Me_3Si^\cdot + Me_3Si^+)/Me_3SiSiMe_3}$; standard potential of the leaving group, $E^0_{Me_3Si^+/Me_3Si^\cdot}$; and the energy of homolytic dissociation of a bond being broken in the process $D(\text{Si—Si})$], are related by the equation obtained from the analysis of the thermochemical cycle of oxidative cleavage of the Si—Si bond:

$$E^0_{(Me_3Si^\cdot + Me_3Si^+)/Me_3SiSiMe_3} = E^0_{Me_3Si^+/Me_3Si^\cdot} + D(\text{Si—Si}) - T\Delta S. \qquad (1)$$

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* Present address: Department of Chemistry, University of Arizona, Tucson AZ 85721, USA.

† *Non-SI units employed*: 1 eV ≈ 9.65 J mol^{-1}; 1 cal ≈ 4.18 J.

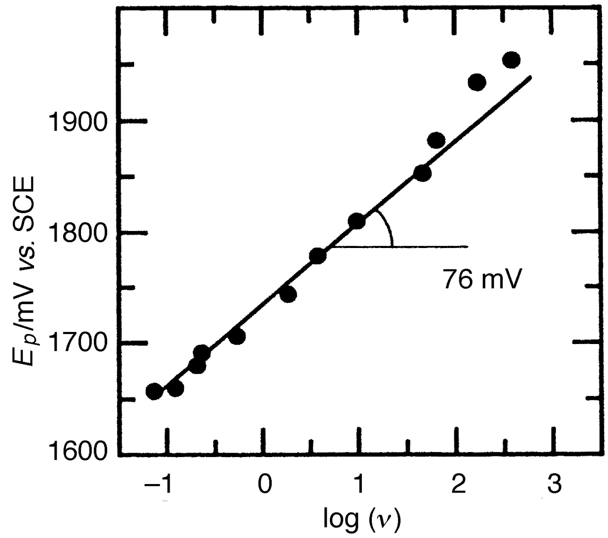

Fig. 1 Oxidation potentials E_p of hexamethyldisilane plotted against log(v); oxidized Pt stationary electrode of 1 mm diameter, concentration of $(Me_3Si)_2$ is 10^{-3} mol l^{-1}; $T = 20\,°C$.

Potentials are taken with a positive sign for oxidation processes; ΔS is the change of entropy for the Si—Si bond dissociation, $\Delta S = S_{Me_3Si\cdot} + S_{Me_3Si\cdot} - S_{Me_3SiSiMe_3}$; for $Me_3SiSiMe_3$ both radical fragments are similar, so $\Delta S = 2S_{Me_3Si\cdot} - S_{Me_3SiSiMe_3}$.

Taking into account the relation between the effective and the standard potentials and assuming the linear approach of the quadratic Marcus equation, one obtains a ratio between D(Si—Si), E_p and $E^0_{Me_3Si^+/Me_3Si\cdot}$, similar to that derived for the reduction of organic halides:[12]

$$D(\text{Si—Si}) \cong 2/3(E_p - E^0_{Me_3Si^+/Me_3Si\cdot}) + [2/3(2\Delta G^{\ddagger} - \lambda_0/2 + T\Delta S - \phi_0)] \quad (2)$$

or

$$D(\text{Si—Si}) \cong 2/3(E_p - E^0_{Me_3Si^+/Me_3Si\cdot}) + C, \quad (3)$$

where λ_0 and ϕ_0 are the solvent reorganization energy and the outer Helmholtz plane potential, respectively.

The value of C was shown to vary slightly within the interval 0.25–0.3 eV for a large number of organic halogen compounds (AlkX, $ArCH_2X$, *etc.*).[13,14] Now, taking for C an average value 0.27 and using the known value D^0_{298}(Si—Si) = 3.49 eV,[15] one obtains the value of the standard oxidation potential of the leaving group (Me_3Si^+ cation) $E^0_{Me_3Si^+/Me_3Si\cdot} = -3.19$ V. This value is very negative and for this reason the oxidation of silyl radicals to silicenium cations has a large driving force throughout most of the range of accessible potentials and the process keeps its two-electron character for all sweep rates.

Using eqn. (1) and taking $T\Delta S$ equal to -0.25 eV (the maximal value for such processes[13]), one obtains the standard potential of dissociative oxidation of hexamethyldisilane $E^0_{(Me_3Si\cdot + Me_3Si^+)/Me_3SiSiMe_3} = 0.525$ V. This value is 1 V less positive as compared to the effective potential E_p and this fact is in good agreement with the dissociative character of the process.

The theoretical value of the transfer coefficient α, calculated for the sweep rate $\nu = 0.1$ V s^{-1},[16] is 0.32, whereas the experimental value, derived from the peak width, was found to be 0.38. Such a reduced value is related to the overestimation of the reorganization factor λ_0 because of an uncertainty in the size of the Me_3Si fragment taken for the calculation. Since the trimethylsilicenium cation does not exist in a "free" form in solution, its hard sphere effective radius is substantially larger than that corresponding to its own size. This fact provokes a decrease of λ_0 and, therefore, the observed increase in α.

The oxidation of hexamethyldisilane has been studied under sonication with high (500 kHz) and low (20 kHz) frequencies. Low frequency ultrasounds caused a total increase of the oxidation current but the shape of the signal was not very informative (Fig. 2). When oxidizing the disilane under sonication by high frequency ultrasounds, the process was characterized by practically the same value of the oxidation potential as in the absence of ultrasounds at a freshly depassivated electrode (Fig. 2). It was shown that several consecutive sweeps do not cause a shift of the oxidation peak towards more positive potentials as in the case of non-sonochemical oxidation. Besides this, there were no changes in the electrochemical behaviour, so this phenomenon can probably be attributed to the cleaning of the electrode surface. We did not succeed in evaluating the parameters for the characteristic dependencies of the oxidation of hexamethyldisilane under sonication with high frequency (500 kHz) ultrasounds because of the low precision of the measurements under these conditions. According to the Levich equation, the growth of the limiting current upon sonication corresponds to an increase of the rotation speed of a conventional rotating disk electrode of the same surface by approximately 1600 times (Fig. 2). The oxidation potential (at least $E_{p/2}$) remains practically unchanged. Thus, no evidence for influence of ultrasounds on the characteristics of dissociative oxidation of hexamethyldisilane was obtained.

Electroreduction of chlorotrimethylsilane

The cathodic process—conventional and sonoelectrochemical reduction of chlorotrimethylsilane—has been considered as well. Usually, in order to obtain a well-shaped reduction peak of chlorotrimethylsilane, one must operate under inert atmosphere using a freshly distilled solvent, vacuum-dried supporting salt and activated Al_2O_3. Even doing so, the reduction signal is observable during several minutes only. After 5–10 min it transforms into another signal, presumably attributed to the reduction of a hydroxy or a fluoro derivative. When a fluoro-containing supporting electrolyte is used in an anhy-

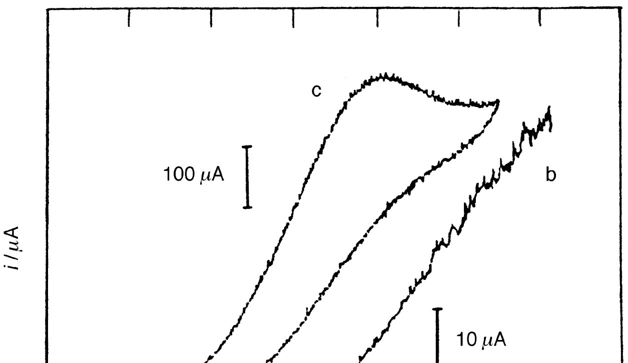

Fig. 2 Voltammograms of the oxidation of $(Me_3Si)_2$ ($C = 10^{-3}$ mol l^{-1}) at a Pt oxidized stationary electrode; CH_3CN–0.01 M Bu_4NBF_4, $\nu = 1$ V s^{-1}, $T = 20\,°C$. (*a*) without ultrasound; (*b*) and (*c*) upon sonication at 20 and 500 kHz, respectively.

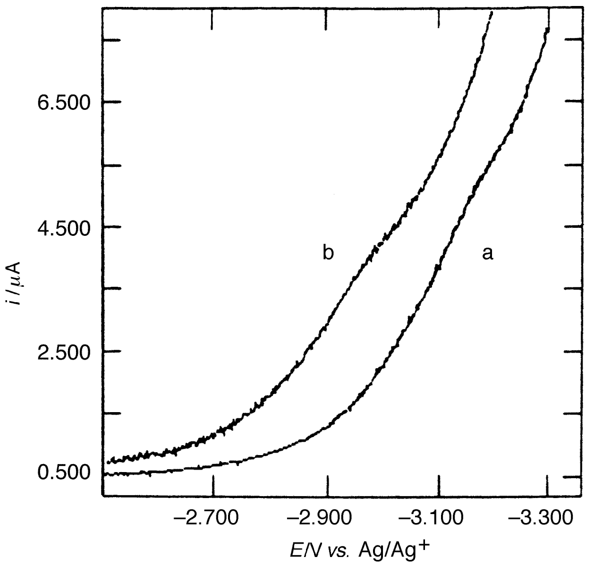

Fig. 3 Voltammograms of the reduction of Me_3SiCl ($C = 8 \times 10^{-3}$ mol l^{-1}) at a Pt oxidized stationary electrode; CH_3CN–0.1 M Me_4NBF_4, $v = 1$ V s^{-1}, $T = 20\,°C$. (*a*) without ultrasound; (*b*) upon sonication at 500 kHz.

drous solvent, it is probably the Cl–F exchange that provides the fluorosilane.[17,18] This exchange is promoted by nucleophilic solvents or by Lewis acids. Fluoride ion arises from the supporting salt anion as the Cl–F exchange reaction consuming F^- progressively displaces the equilibrium of its formation from BF_4^-.

Upon reduction in CH_3CN–0.1 M Me_4NBF_4 media without ultrasounds, chlorotrimethylsilane shows a quite distinguishable signal. The peak current, i_p, is linear with concentration when $C > 5 \times 10^{-3}$ mol l^{-1} and the ratio $i_p\ v^{-1/2}$ remains constant within the range of sweep rates 0.05–20 V s^{-1}, indicating a diffusional or quasi-diffusional character of the process. The high negative reduction potential ($E_p = -2.68$ V *vs.* SCE), as well as the high dissociation energy of the Si—Cl bond, the number of electrons $n = 2$ and $\alpha = 0.29$ suggest the dissociative character of the electron transfer in the reduction of this compound.

The estimation of the standard potential $E^0_{Me_3SiCl/Me_3Si^\cdot + Cl^-}$ using eqn. (1) and the known gas phase bond dissociation energy for the Si—Cl bond [D(Si—Cl) = 5.49 eV[19]] provide the standard potential for the dissociative reduction of this compound, $E^0_{Me_3SiCl/Me_3Si^\cdot + Cl^-}$, as about -3.3 V. Since the reduction occurs at a less negative potential than the calculated standard potential, the reductive cleavage of the Si—Cl bond most probably includes a substantial polarization of this bond in a polar solvent and/or a preceding (or simultaneous) interaction with the cation of the supporting electrolyte. By weakening and lengthening the Si—Cl bond, both these factors lower the effective bond strength D(Si—Cl) with respect to its value in the gas phase.

The effective Si—Cl bond energy, estimated according to eqn. (3) (taking $E^0_{Cl^\cdot/Cl^-} = 1.89$ V, $C = 0.27$ eV[13] and $E_p = -2.68$ V), should be as large as 3.3 eV or about 76 kcal mol^{-1}. Evidently, some interactions, like pre-dissociation or ion-pair formation, and the increasing electrophilicity of silicon in the chlorosilane in solution play an important role during the electroreduction of Me_3SiCl. In the absence of such interactions this chlorosilane would not be reducible at all because it would have had a peak potential $E_p \cong -(5.49 \times (3/2) - 0.27 - 1.89) = -6$ V. Given that the Si—F bond is stronger than the Si—Cl bond, similar factors probably take place in the reduction of fluorosilanes too. Indeed, at the observed reduction potential ($E_p = -3.15$ V) and the standard potential of the leaving group ($E^0_{F^\cdot/F^-} = 2.62$ V[13]), the effective Si—F bond energy should have the value $D(\text{Si—F}) = (2.62 + 3.15)(2/3) + 0.27 = 3.58$ eV or about 82 kcal mol^{-1}.

When tracing reduction curves of chlorotrimethylsilane upon sonication ($f = 500$ kHz), the signal of the chlorosilane does not shift, but the signal of a fluoro derivative appears a few seconds after ultrasounds are applied (Fig. 3). The chlorosilane peak disappears and no peak at less negative potentials is observed. Apparently, the action of the ultrasounds is purely kinetic and consists in acceleration of the Cl–F exchange, while the concentration of residual water is not large enough to compete with the F^-anion, which is, in addition, known to be a weak nucleophile.

It is to be noted that ultrasonic intensification of electrochemical processes involving chlorosilanes (even the processes of "anodic reduction"[20]) are widely used for the electrosynthesis of carbosilanes[21,22] but no phenomena related to the thermodynamics of the process were reported.

Experimental

The oxidation of hexamethyldisilane (Aldrich) was carried out in a CH_3CN–0.01 M Bu_4NBF_4 solution at an oxidized platinum electrode using a PAR-273 potentiostat. The auxiliary electrode was a Pt wire and the reference electrode was a SCE. For the reduction of chlorotrimethylsilane, the reference electrode was separated from the analyte by an electrolytic bridge filled with a 0.1 M solution of Me_4NBF_4 in CH_3CN in order to prevent AgCl formation at the tip of the reference electrode. Acetonitrile (Aldrich) was distilled over CaH_2 immediately prior to use. Ultrasonic experiments were carried out in a previously described[23] Teflon cell of 60 ml using a PAR-273 potentiostat and an ultrasonic generator (Sonic and Materials, Inc., Connecticut). The ultrasonic power at 20 kHz, as measured by calorimetry, was 2.4 W cm^{-2}. At 500 kHz, the output power of the generator was 20 W, which, given the bottom area of the cell equal to 19.63 cm^2, approximately corresponds to an apparent total power of 1 W cm^{-2}.

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