

ELECTRODIC PROCESSES OF DERIVATIVES OF 2,2,4,4 - TETRAMETHYLPENTANE ON STATIONARY SOLID ELECTRODES. I. CYCLIC VOLTAMMETRY OF 3-HYDRAZONES OF 2,2,4,4-TETRAMETHYLPENTANE

By

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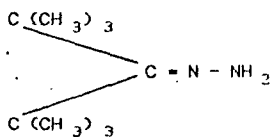
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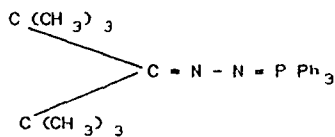
3-Hydrazo-2.2.4.4-tetramethylpentane and 3-triphenylphosphoranilideno-hydrazo-2.2.4.4-tetramethylpentane in acetonitrile and N.N-dimethylformamide by means of cyclic voltammetry on stationary solid electrodes (glassy carbon, Pt and Au) were studied. The catalytic effects of the nature and state of the electrode surface and the solvent were investigated. Mechanisms were suggested for the redox reactions that these compounds undergo cathodic reduction and anodic oxidation. The potentials of the respective processes, the diffusion coefficients, the observed standard rate constants and the electrode transfer coefficients were determined.

Introduction

This work deals with the electrodic oxidation and reduction of 3-hydrazones of 2.2.4.4-tetramethylpentane:



I



II

I: 3-hydrazo-2.2.4.4-tetramethylpentane.

II: 3-triphenylphosphoranilidenohydrazo-2.2.4.4-tetramethylpentane.

The electrode reactions were carried out in acetonitrile (AN) and N,N-Dimethylformamide (DMF), with Bu_4NClO_4 (10^{-1} mol. dm^{-3}) as a supporting electrolyte.

Compounds I and II were synthesized and examined some time [1-4]. The products of their chemical oxidation are the corresponding azines [5, 6].

The electrochemical reduction of the hydrazones was examined polarographically in acid and neutral aqueous solutions [7-9]. The oxidation of keto-arylhydrazones in water-AN solutions gives the appropriate ketones, while the oxidation of cyclic hydrazones such as 3.5.5-trimethyl-2-pyrazoline gives 3.3-dimethylbutan-2-one [10].

The electrooxidation of hydrazones on the platinum electrodes in non-aqueous AN was described by Barbey et al. [11] and Chiba et al [12]. Barbey oxidized 3-hydrazo-dibenzophenone voltammetrically, while Chiba oxidized its phenyl-substituted derivatives ($x = -\text{H}$; $-\text{CH}_3$; $-\text{OCH}_3$; $-\text{Cl}$) amperometrically.

In both cases, platinum electrode were used as working electrodes, and the almost identical experimental conditions (LiClO_4 as a supporting electrolyte, concentration of hydrazones in mmol. dm^{-3} range) permit acceptance of the suggestion [11, 12] as a basis for discussion in this work.

In both works the corresponding azines were obtained as final products, whereas there were different proposals concerning the mechanisms of the reaction, depending on the composition of the solution, the experimental conditions and the nature of the electrode.

Experimental

Cyclic voltammetry (CVC) on compounds I and II was carried out by using the Wenking ST-72 apparatus and, the XY Houston Instruments 2000 recorder with IR_e compensation.

The CVC measurements were conducted in the range of the sweep potential polarization rate from $v = 0.010 \text{ V}\cdot\text{s}^{-1}$ to $v = 0.400 \text{ V}\cdot\text{s}^{-1}$ in the classical thermostatic (298 ± 0.5) K and hermetic vessel of 90 cm^3 volume made by METROHM.

The following working electrodes were used:

- A polished glassy carbon electrode (GCE) SIGRI with geometrical surface area $A_1 = (0.44 \pm 0.02) \text{ cm}^2$, put in the epoxide-glassy holder with the electric contact. Before each measurement, the electrode was polished with the diamond pastes of 30, 6, 3 and $1 \mu\text{m}$ and Al_2O_3 of $0.05 \mu\text{m}$ and it was then rinsed with acetone, triple distilled water, and finally ether-dried. The GCE was then prepared electrochemically according to the literature [13-16].

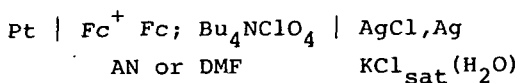
- A polished platinum electrode (Pt_{pol}) with a geometrical area $A_2 = (0.44 \pm 0.02) \text{ cm}^2$ prepared as the GCE.

- A polycrystalline gold electrode (Au_{app}) with a geometrical area $A_3 = (0.09 \pm 0.02) \text{ cm}^2$. Golden wire with $\phi = 0.15 \text{ cm}$ was put in a teflon holder after baths in concentrated HNO_3 and in triple distilled water and was prepared for the

measurements by means of the sweep potential rate method, i.e. by cyclic polarization method, in the range from the hydrogen evolution potential to the oxygen evolution potential in an aqueous solution of HClO_4 ($5.10^{-1} \text{ mol.dm}^{-3}$).

After production of the "model" polarization curve [17, 18], the Au_{app} electrode was used for measurements. This method permitted reproducibility of measurements within $\pm 0.5 \%$ [19]. In relation to the surface of the polished electrode, the stabilized electrode Au_{app} has a surface development coefficient of $4.0 \div 4.1$ [20]. In this way, the surface area Au_{app} is close to the surfaces of A_1 and A_2 .

The auxiliary electrodes were made of platinum mesh and were separated from the working part of the electrolyte by diaphragm of porous glass. In all measurements, the AgCl/Ag electrode in KCl_{sat} aqueous solution (METROHM) was used as a reference electrode in AN and DMF. All the potential values given in this work are referred to the reference electrode used. To allow a comparison of the measured potentials with the results obtained in the other solvents, additional measurements were carried out with reference to the "ferrocene potential scale" [21, 22] it is commonly used. The CVC loop ($v = 0.100 \text{ V.s}^{-1}$) was registered in the following system:



The formal potential values:

$$E_f^{\text{O}} = 1/2 (E_{\text{p,a}} + E_{\text{p,c}}) \text{ were equal} \\ \text{DMF } E_f^{\text{O}} = (0.450 \pm 0.005) \text{ V vs ref. electrode,}$$

$$AN_{E_f}^O = (0.500 \pm 0.005) \text{ V vs ref. electrode,}$$

in accordance with the literature [23].

The examined compounds readily undergo hydrolysis or redox reactions in the presence of minute quantities of water or oxygen.

In the presence of water > 0.05 w %, the compound II is reduced irreversibly to phosphazine. Accordingly, the water was carefully removed from the supporting solutions with molecular sieve 4A and freezing-out in liquid nitrogen, and they were forced through to the measurement cell using argon. The glass ampoule with the examined compound was crushed in the cell where the overpressure of dry argon was kept. The outlet of argon was possible with the appropriate syringe.

Compounds I and II were examined at concentrations of $4.2 \cdot 10^{-3}$, $9.3 \cdot 10^{-3}$ and $2.54 \cdot 10^{-2}$ mol.dm⁻³, $1 \cdot 10^{-3}$ mol dm⁻³ tetrabutylperchlorate (Bu₄NClO₄) was used as a supporting electrolyte. The measurements were conducted in the range of the sweep potential polarization rate from $v = 0.02 \text{ V} \cdot \text{s}^{-1}$ to $v = 0.200 \text{ v} \cdot \text{s}^{-1}$.

Analysis of the CVC curves was carried out according to Nicholson and Shain [24, 25]. The function of irreversibility $\psi = f(\Delta E_p)$ for calculating the observed rate constant (k_s) was calculated from polynomial:

$$\Delta E_p = a \psi + b \psi^{-1} + c \psi^{-1/2} + \dots$$

where: $a = 20.615$; $b = -1.40167$; $c = 3.4033 \text{ E-2}$;
 $d = -3.37491 \text{ E-4}$; $e = 3.79258 \text{ E-7}$; $f = 1.74068$
 E-8 ; $g = -9.4157 \text{ E-11}$; $h = -1.70248 \text{ E-13}$;
 $i = 1.84194 \text{ E-15}$; $j = 5.54909 \text{ E-19}$.

The application of this equation gave results compatible with the calculation using Heinz's [26] suggestion for $\Delta E_p = 80 \div \div 150$ mV within the limits of the mean square error of the average value.

Results and discussion

The CVC curves of compound I on the stationary solid electrodes in AN are presented in Figs. 1-3. In the cathodic process hydrazone I is reduced irreversibly at a potential $E_{p,c} = 0.5 \div -1.1$ V (depending on the type of the electrode) according to the scheme after [7-10]:

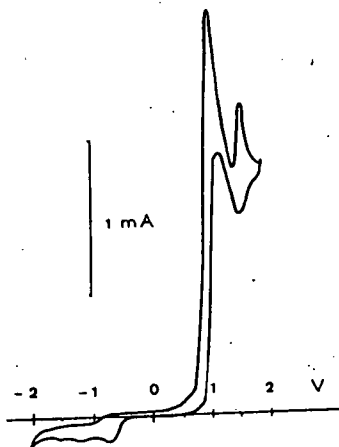
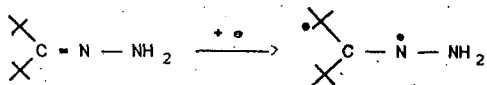


Figure 1.: Cyclic voltammogram of compound I in acetonitrile on glassy carbon electrode. Supporting electrolyte: $1 \cdot 10^{-1}$ mol dm^{-3} Bu_4NClO_4 ; $C_I = 2.54 \cdot 10^{-2}$ mol dm^{-3} ; $v = 0.100$ V s^{-1} .



It has been pointed out that this reaction is independent of the anodic reactions that compound I undergoes. The electrochemical processes occur in the range of the $+0.7 \div +1.8$ V polarization potentials.

For the electrooxidation of hydrazones, Chiba [12] proposes with the separation of nitrogen and the suggested of

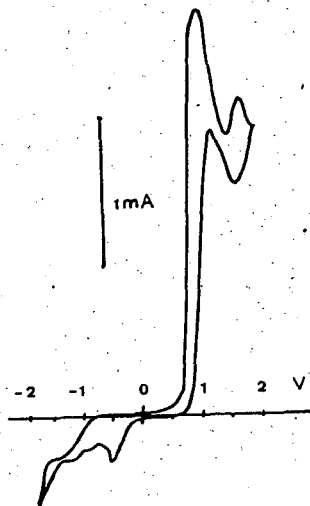
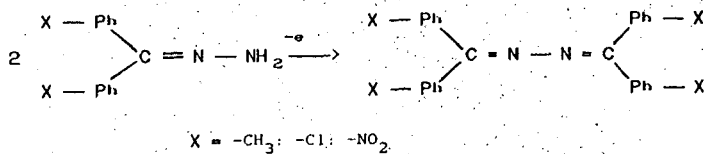
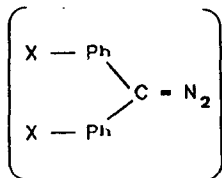


Figure 2.: Cyclic voltammogram of compound I in acetonitrile on polished platinum electrode; other parameters as in Fig. 1.

transitory formation:



The amperostatically performed electrooxidation proceeds in the potential range $+0.7 \div +2.0 V_{sce}$. The development of a potential of $+2.0 V_{sce}$ by the working electrode was regarded [12].

As seen in Figs. 1-3, all the electrooxidation processes proceed in a similar range of potentials $\pm 50 \text{ mV}$, but their voltammetric characteristics are more precise.

Analysis of the CVC curves according to [24, 25] reveals the possibility of the following processes occurring in the range of the polarization potentials:

1. adsorption - desorption of substrates and reaction products;
2. the electrochemical reaction of electron transfer precedes the chemical reaction of dimerization;
3. the overall reaction is irreversible and its products are not reduced.

Similarly as in [12] the appearance of yellow crystals was observed. After purification in cool AN, they were identified (IR spectroscopy) as tetramethylpentane diazine.

Thus, the mechanism suggested by Barbey et al. [11] seems

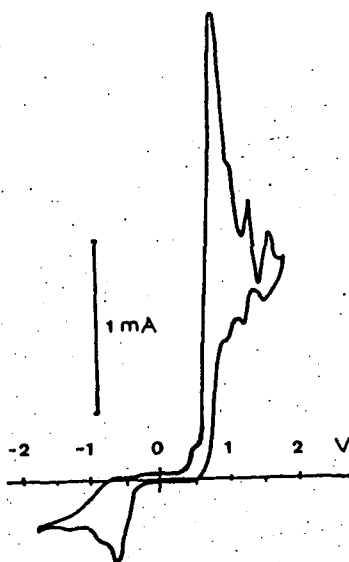
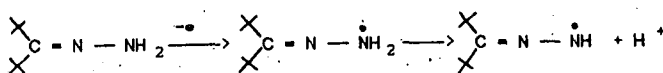
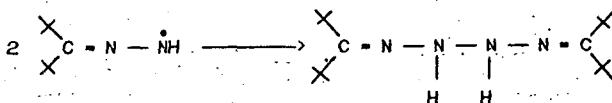


Figure 3.: Cyclic voltammogram of compound I in acetonitrile on the activated gold electrode. Other parameters as in Fig. 1.

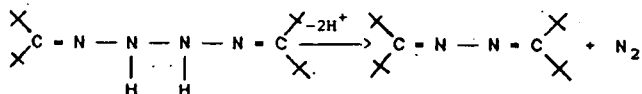
to be more probable:



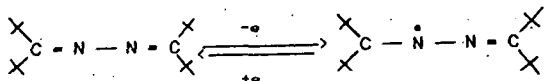
Then:



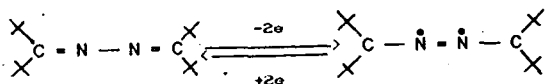
and finally:



Moreover, in the potentials interval $+1.5 \div 1.8$ V in Figs 1-3. the loop probably relating to the reaction of electron transfer is visible:



or



In DMF the CVC curves on gold and platinum electrodes permit separation of the CVC loop (Fig. 4), suggesting the possibility of quasi-reversible reactions at potential $E_f^0 = (-0.800 \pm 0.02)$ V:

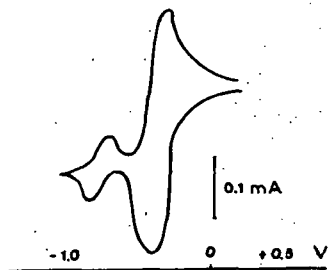
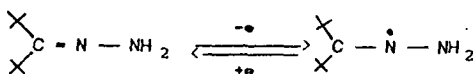


Figure 4.: Cyclic voltammogram of compound I in DMF on polished platinum electrode: $c_I = 9.3 \cdot 10^{-3}$ mol·dm⁻³; $v = 0.04$ Vs⁻¹



with the parameters calculated for the polished platinum electrode:

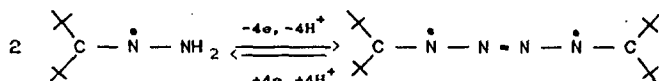
$$D_{\text{Ox}} = (1.1 \pm 0.04) \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$$

$$D_{\text{Red}} = (1.0 \pm 0.03) \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$$

$$\alpha n_{\alpha} = (0.064 \pm 0.04)$$

$$k_s = (1.24 \pm 0.11) \cdot 10^{-4} \text{ cm s}^{-1}$$

At potential $E_f^0 = (-0.315 \pm 0.05) \text{ V}$ on Pt_{pol} we have:



with parameters:

$$D_{\text{Ox}} = (2.3 \pm 0.08) \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$$

$$D_{\text{Red}} = (1.1 \pm 0.05) \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$$

$$\alpha n_{\alpha} = (0.66 \pm 0.04)$$

$$k_s = (2.60 \pm 0.31) \cdot \text{cm} \cdot \text{s}^{-1}$$

At potentials $> +0.7 \text{ V}$ the irreversible chemical reaction of formation of diazine proceeds. The current value for this reaction is constant in the range $+0.7 \div +1.6 \text{ V}$. and is independent of the sweep potential polarization rate. The presence of diazine was proved as in works [11, 12].

The electrodic processes of phosphoranilidenohydrazone II proceeded similarly to those of I. proving both the catalytic influence of the nature and the surface of the electrode and the influence of the solvent on the examined

process.

The influence of the solvent is visible both in the dependence on Gutmann's donor number $^{AN}DN = 14.1$; $^{DMF}DN = 27.0$. and on the ability to create strong solvates (AN) or the nature of the interaction with compounds containing an active hydrogen atom (DMF).

Figure 5 exemplifies the CVC curve of a hydrazone. This CVC curve on a platinum electrode suggests a process close to the quasi-reversible reaction with a potential $E_f^O = (-0.25 \pm 0.01)$ V and the two-stage ($E_{p,a} = +0.7$ V and $E_{p,a} = +1.25$ V) irreversible electrochemical-chemical process.

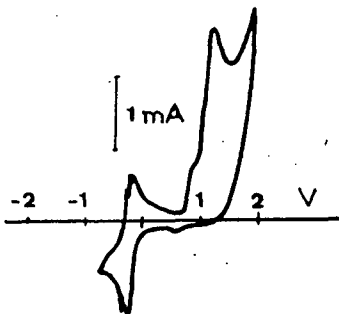


Figure 5.: Cyclic voltammogram of compound II in AN on the activated gold electrode; $v = 0.100 \text{ Vs}^{-1}$; $c_{II} = 2.54 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

The process with a formal potential $E_f^O = -0.25$ V is a quasireversible reaction connected with the adsorption - desorption of substrates and reaction products. This was indicated by the additional small peaks visible below $E_{p,c}$ on the cathodic branch and in front of the $E_{p,a}$ peak on the

anodic branch of the CVC loop. Thus, Nicholson and Shain's model cannot be applied to calculate the parameters of this electrodic reaction.

Change of the solvent to DMF clearly revealed the influence both of the electrode material and of the nature of the solvent on the electrodic processes of compound II (Fig. 6).

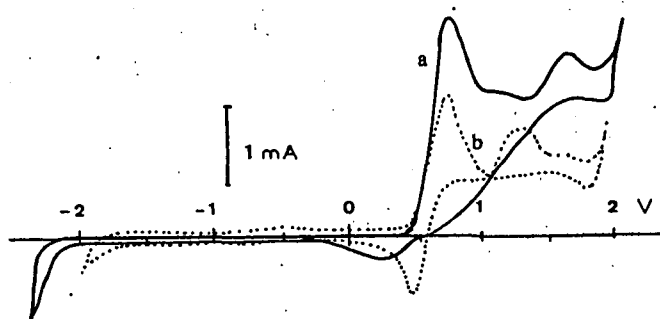


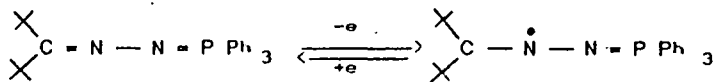
Figure 6.: Cyclic voltammogram of compound II in DMF on the glassy carbon electrode (a) on platinum (b); other parameters as in Fig. 5.

Complex anodic processes were studied both on the GCE electrode curve (a) and on the platinum electrode (b). Owing to the lack of the active group ($=N-NH_2$), this hydrazone does not undergo reduction in the whole range of cathodic polarization.

On the plished platinum electrode, the separated CVC loop yielding the formal potential of the process.

$E_f^0 = (+0.610 \pm 0.02)$ V. fulfils the criteria of quasi-reversibility.

Thus, the following equation may be suggested for electrodic reaction:



with parameters:

$$D_{\text{Ox}} = (1.57 \pm 0.33) \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1},$$

$$D_{\text{Red}} = (1.88 \pm 0.35) \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1},$$

$$\alpha n_{\alpha} = (0.74 \pm 0.06)$$

$$k_s = (9.70 \pm 0.36) \cdot 10^{-5} \text{ cm} \cdot \text{s}^{-1}$$

The processes in the range of the potentials +1.1 + + 1.8 V are independent of the sweep potential polarization rate.

Conclusions

1. The electrodic processes of 3-hydrazo-2.2.4.4-tetramethylpentane I and 3-triphenylphosphoranilidenohydrazo-2.2.4.4-tetramethylpentane II are dependent on the nature and the catalytic activity of the electrode and on the properties of the solvent.

2. The quasi-reversible electrodic processes of I and II on the platinum and gold electrodes in DMF allowed calculation of the basic parameters of the reaction: the diffusion coefficients D_{Ox} and D_{Red} , the electron transfer coefficient αn_{α} and the observed standard rate constant k_s .

3. The processes of anodic oxidation proceed according

to the suggested mechanism. As a result of anodic oxidation, I gives the corresponding diazine. It was not possible to separate the products of the anodic reaction of compound II.

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ЭЛЕКТРОДНЫЕ ПРОЦЕССЫ ПРОИЗВОДНЫХ 2,2,4,4-ТЕТРАМЕТИЛПЕНТАНА
НА НЕПОДВИЖНЫХ ТВЕРДЫХ ЭЛЕКТРОДАХ. I. ЦИКЛИЧЕСКАЯ ВОЛЬТАМЕТ-
РИЯ 3-ГИДРАЗОНОВ 2,2,4,4-ТЕТРАМЕТИЛПЕНТАНА

Х. Шолл и П. Кричмоник

Изучены методом циклической вольтометрии на неподвижных твердых электродах (Сс) ($Pt_{пол}$) и ($Au_{алл}$) 3-гидразо-2,2,4,4-тетраметилпентан и 3-трифенилфосфоранилидено-2,2,4,4-тетраметилпентан в ацетонитриле и в N,N' -диметилформамиде. Характеризованы каталитическое действие материала и состояния поверхности электрода, а также растворителя на протекающие процессы. Предложены механизмы окислительно-восстановительных реакций, происходящих при катодном восстановлении и анодном окислении изучаемых соединений. Определены значения потенциалов для соответствующих процессов, величины диффузионных коэффициентов и электронных передач. Определены также стандартные коэффициенты скоростей реакций.