Spin-adduct of the P_4 ⁻ radical anion during the electrochemical reduction of white phosphorus

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> The radical anion P_4 ^{•-} was detected and identified by the ESR method as a spin-adduct with nitrone during the electrochemical reduction of white phosphorus in the presence of a spin trap, *viz.*, α -phenyl-*N*-*tert*-butylnitrone, in a special electrolysis cell with a helical platinum working electrode in the potentiostatic mode. The character of the behavior of P_4 ^{•-} and the spin trap during electrochemical reduction was monitored by cyclic voltammetry directly in the electrolysis cell, and the spin-adduct formed was detected by ESR.

Key words: white phosphorus, electrochemical reduction, ESR, radical anion, spin-adduct.

The problem of the selective cleavage of the P-P bonds in a white phosphorus molecule is very important in the chemistry of phosphorus-containing compounds.^{1,2} The radical character of the cathodic reduction of white phosphorus has been assumed earlier.³ However, such products of activation of P_4 have not yet been detected. The purpose of the present study was to observe the primary products of cathodic reduction of a P₄ molecule. To create a necessary concentration of paramagnetic species in the resonator of an ESR spectrometer, we used a special cell with the helical working electrode.⁴ The method of spin traps^{5,6} based on the reaction of electrochemically inactive α -phenyl-*N*-tert-butylnitrone (1), resulting in the stable nitroxyl radical (Scheme 1), was used to detect radical anion species. The stable nitroxyl radical can be identified by ESR spectroscopy.



Experimental

Benzene was dehydrated by distillation over sodium. α -Phenyl-*N-tert*-butylnitrone (1) and Et₄NBF₄ (Fluka) were used without additional purification. Acetonitrile was purified by triple distillation over KMnO₄ and P₂O₅, and Et₄NBF₄ was dried *in vacuo* for 2 days at 100 °C. Dimethylformamide was distilled, kept for 12 h over calcined K₂CO₃, then distilled repeatedly over CaH₂, and stored over molecular sieves 3A calcined at 300 °C. A solution of white phosphorus in benzene ($\sim 1.6 \cdot 10^{-2} \text{ mol } \text{L}^{-1}$) was purged with helium through a capillary immersed to the bottom of the cell. The material of the working and auxiliary electrodes was platinum, and Ag/AgNO₃ (0.01 mol L⁻¹) was a reference electrode.

Measurements were carried out using the program-apparatus complex⁷ mounted on the basis of an analog-electrochemical setup with a PI-50-1 potentiostat, a Pr-8 programmer, an X-range ESR spectrometer (Radiopan), and E14-440 analog-todigital and digital-to-analog converter (L-Card), and a computer.

The WinSim 0.96 program (NIEHS) was used for ESR spectra processing.

The images of the films were obtained on a HITACHI TM-1000 scanning electron microscope.

Results and Discussion

The curves obtained by cyclic voltammetry (CV) at the Pt electrode for a solution of compound 1 in MeCN $(0.01 \text{ mol } L^{-1})$ and a solution of white phosphorus in a benzene-MeCN (1 : 1) mixture vs 0.1 M solution of Et_4NBF_4 are shown in Fig. 1. To exclude the formation of products of phosphorus oxidation and hydrolysis, all procedures were carried out in a thoroughly dehydrated solvent. It should be mentioned that the compounds containing the mobile hydrogen atom give no pronounced reduction peaks on Pt down to potentials of the supporting electrolyte discharge. The CV curves of a solution of white phosphorus at a potential of -1.5 V contain the irreversible peak corresponding to its reduction. Thus, the reduction peak close to the one-electron peak (estimated by the comparison with benzophenone used as standard) relates to the electron transfer to a white phosphorus molecule to form radical anions P_4 .

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Fig. 1. CV curves of a 0.01 *M* solution of nitrone **1** in MeCN vs 0.1 M solution of Et₄NBF₄ (*I*) and white phosphorus solution in a benzene—MeCN (1:1) mixture against the same background after helium purging for 10 min (*2*) (*T* = 298 K, Pt electrode, $v = 0.1 \text{ V s}^{-1}$).



Fig. 2. Experimental (1) and simulated overall (2) ESR spectra of the spin-adducts detected upon the reduction of white phosphorus and a 1 *M* solution of nitrone 1 in a benzene—MeCN (1 : 1) mixture *vs* 0.1 *M* solution of Et_4NBF_4 after helium purging for 10 min and the ESR spectra of their constituent spin-adducts: 1.1⁽³⁾, 1.1⁽⁺⁾ (4), and 1.P₄⁽⁻⁾ (5).

There is a large data bank on the ESR spectra and magnetic resonance characteristics of spin-adducts of compounds belonging to various classes.* In particular, the spin-adduct of the short-lived phosphorus-centered radical •PHO₂⁻ and nitro-

$$\begin{array}{c}
H \\
Ph-C-N-CMe_{3} \\
P \\
P \\
P \\
P^{-P} \\
P^{-P} \\
P^{-} \\
\mathbf{1} \cdot P_{4}^{--}
\end{array}$$

ne **1** was obtained⁸ by the electrochemical oxidation of hypophosphite on the nickel electrode. The following magnetic resonance parameters of the spin-adduct were detected: $a_{\rm N} = a_{\rm P} = 15.91$ G, $a_{\rm H-CH} = 1.99$ G, $a_{\rm H-PH} = 3.21$ G, g = 2.0060. However, no spin-adducts of the P₄⁻⁻ radical anion were studied. The reduction peak of nitrone

1 is by ~1 V more negative than the reduction peak of P_4 (see Fig. 1). Therefore, this trap was used for the detection of white phosphorus radical anions. The experimental ESR spectrum of the spin-adduct detected upon the reduction of white phosphorus (~1.6 \cdot 10⁻² mol L⁻¹) in the potentiostatic mode at a potential of -1.5 B and a 1 *M* solution of nitrone 1 in a benzene —MeCN (1 : 1) mixture at the Pt electrode vs 0.1 *M* solution of Et₄NBF₄ is shown in Fig. 2.



Fig. 3. View of the polyphosphorus films upon the electrochemical reduction of P_4 in DMF vs 0.1 *M* solution of Et_4NBF_4 detected with a HITACHI TM-1000 microscope with a magnification of 200 (*a*), 2000 (*b*), and 10 000 times (*c*).

^{*} http://epr.niehs.nih.gov.







Fig. 4. View of the polyphosphorus films upon the electrochemical reduction of P_4 in an aqueous solution of HCl detected with a HITACHI TM-1000 microscope with a magnification of 2000 (*a*), 4000 (*b*), and 10 000 times (*c*).

The ESR spectrum also exhibits two spin-adducts of free radicals of the spin trap 1·1' with the hyperfine coupling constants (HFC) $a_{\rm N} = 13.59$ G, $a_{\rm H} = 2.22$ G and $a_{\rm N} = 18.60$ G, $a_{\rm H} = 4.00$ G for the first and second adducts, respectively, with the ESR linewidths $\delta H = 0.65$ G. The ESR spectrum of spin adduct 1·P₄⁻⁻ has the following parameters: $a_{\rm N} = 14.10$ G, $a_{\beta-\rm P} = 14.6$ G, $a_{\rm H} = 0.80$ G, $a_{\gamma-\rm P} = 0.78$ G, and $\delta H = 0.65$ G. The HFC constants $a_{\beta-\rm P}$

and $a_{\gamma-P}$ were attributed to the phosphorus atom in the β -position and two equivalent phosphorus atom nuclei in the γ -positions to the radical center, respectively.

During several first minutes after the beginning of electrolysis, the lines of the experimental spectrum begin to broaden and the pattern changes gradually, indicating the formation of polymer products.

The formation of polymer products upon the electrochemical reduction of white phosphorus in DMF vs 0.1 Msolution of Et₄NBF₄ at E = 2.1 V and $C_{P_4} = 5 \cdot 10^{-2}$ mol L⁻¹ is confirmed by the microscopic images of the electrode surface (Figs 3 and 4). The view of the polyphosphorus films depends on the electrolysis conditions and duration. The polyphosphorus products formed at the Pt electrode in DMF are rapidly dissolved and desorbed to the electrolyte volume. At the same time, on the lead cathode in DMF they form a black sponge nanoporous film (see Fig. 3). In a water-containing electrolyte, a black polyphosphorus conducting film is also formed, but the structure of polyphosphides is filamentous and needle-like in this case (see Fig. 4). The thickness of the polymer filaments is ~1 µm.

Thus, the P_4 ⁻⁻ radical anion was detected for the first time in the potentiostatic mode by the ESR method as the spin-adduct with α -phenyl-*N-tert*-butylnitrone in the electrochemical reduction of white phosphorus in the electrolysis cell with the helical platinum working electrode. The present study confirms the radical character of the intermediates of white phosphorus described earlier.³

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