Electrooxidation of 2,3-dihydro-1*H*-1,3,2-diazaphospholes

V. V. Yanilkin, V. I. Morozov, F. F. Nigmadzyanov, T. V. Gryaznova, and A. M. Kibardin*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan', Russian Federation.
Fax: +7 (843 2) 75 2253

Electrooxidation of 2-R-1,3-dibutyl-4,5-dimethyl-2,3-dihydro-1*H*-1,3,2-diazaphospholes with tri- and tetracoordinated phosphorus atoms were studied. Reversible one-electron oxidation gives radical cations at potentials of −0.37 to +0.36 V. Magnetic parameters of the radical cations were measured.

Key words: electrooxidation, ESR, heterocycles, dihydrodiazaphospholes.

In recent years, extensive studies of electrochemical oxidation and reduction of organophosphorus compounds have been carried out.[1] Among cyclic derivatives, attention is attracted by new heterocyclic systems, dihydro-1,3,2-diazaphospholes. Previous studies of the photoelectron spectra of these compounds have shown that they are characterized by low first ionization potentials.[2] This suggests that they easily undergo chemical or electrochemical oxidation. In fact, dihydro-1,3,2-diazaphospholes are oxidized by air oxygen under mild conditions:[3] 2-alkyldihydro-1,3,2-diazaphospholes are converted into 2-oxo-derivatives, and 1,3-dibutyl-2-ethoxy-4,5-dimethyldihydro-1,3,2-diazaphosphole gives 2-butylimino-3-butyl-2-ethoxydihydro-1,3,2-oxazaphosphole.

Electrochemical reactions of compounds of this type have not been reported in the literature. We studied the electrooxidation of 2-R-1,3-dibutyl-4,5-dimethyl-2,3-dihydro-1*H*-1,3,2-diazaphospholes (R = MeO (**1**), Me (**2**), EtO (**3**), Et (**4**)) and 2-R-1,3-dibutyl-4,5-dimethyl-2,3-dihydro-1*H*-1,3,2-λ^5-diazaphosphole 2-oxides (R = EtO (**5**), Et (**6**)) in MeCN at a platinum electrode.

For compounds **1** and **3**—**6**, cyclic voltammograms (CVA) in the temperature range from −35 to 22 °C were recorded. The CVA of derivatives **1**—**3** recorded at room temperature exhibit one irreversible anodic peak, corresponding to the transfer of two electrons per one molecule. At low temperatures (−10 to −35 °C), in addition to the one-electron anodic peaks, which are shifted to less anodic potentials, the corresponding cathodic peaks on the reverse CVA branch can be detected for these compounds. For compound **5**, only one oxidation peak is observed, and for compound **6**, there are two oxidation peaks at any temperature. It can be seen from Table 1 that the heterocyclic compounds studied are oxidized at close potentials. This process is reversible ($\Delta E_p = E_p^{Ox} - E_p^{Red} = 2.2RT/F$) and yields radical cations, which have been detected by ESR spectroscopy. The radical cations are unstable, as indicated by the fact that the relative cathodic current (i_p^{Red}/i_p^{Ox}) decreases as the temperature increases.

The electrochemical reactivity of the studied compounds is largely determined by the type of coordination of the phosphorus atom and the nature of the substituents. Diazaphospholes with tricoordinated phosphorus are oxidized more readily than the corresponding compounds with tetracoordinated phosphorus; however, the

Table 1. Electrochemical characteristics of the first oxidation peaks of compounds **1**, **3**—**6**

Compound	Supporting electrolyte[a]	T /°C	E_p^{Ox} /V	i_p^{Red}/i_p^{Ox}
1	Bu_4NBF_4	−35	−0.05	0.98
		−30	−0.06	0.96
		−12	0.04	0.95
3	$LiClO_4$	−30	−0.01	1.00
		−25	0.00	0.87
		−10	0.06	0.74
		−3	0.10	0.60
	Bu_4NBF_4	−34	0.05	1.00
		−20	0.04	0.97
		−7	0.03	0.98
		+8	−0.05	0.96
4	$LiClO_4$	−30	−0.41	0.90
		−10	−0.36	0.88
	Bu_4NBF_4	0	−0.37	0.92
		+23	−0.36	0.84
		−19	−0.37	1.00
		−8	−0.37	1.00
		+5	−0.41	1.00
5	$LiClO_4$	−32	0.36	0.57
		−18	0.33	0.4
		+10	0.32	0.25
		+22	0.33	0.21
6	$LiClO_4$	−32	0.30	1.00
		−15	0.30	1.00
		−2	0.26	0.96
		+5	0.26	1.00
		+21	0.26	0.89

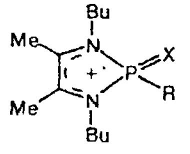
[a] The concentration was 0.1 mol L^{-1}.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1522—1524, August, 1998.

1066-5285/98/4708-1478 $20.00

influence of oxo groups is much less pronounced than that in the case of phosphines.[4] Derivatives with tricoordinated phosphorus atoms are oxidized in the same region of potentials as enediamines.[5] These results confirm the conclusion[2] that the lone electron pair of phosphorus contributes insignificantly to the highest occupied molecular orbital. The sequence of variation of the E_p values for derivatives of tricoordinated phosphorus (OEt > OMe > Et) is consistent with the order in which the oxidation potentials of saturated acyclic and cyclic derivatives of tricoordinated phosphorus change.

Electrooxidation of the diazaphospholes under consideration at first-wave potentials at −30 °C affords, according to ESR spectroscopy, paramagnetic species characterized by complex hyperfine coupling (HFC) with the magnetic nuclei of the heterocycle and the substituents. Electrooxidation of compounds **1**, **3**, and **6** in solution yields unstable radicals, whose magnetic parameters are presented in Table 2. Spectral data point to a symmetrical distribution of spin density in the heterocyclic system. Analysis of the ESR spectra makes it possible to suggest that oxidation of compounds **1**, **3**, and **6** in solutions gives type **7** radical cations, similar to the radical cation derived from vinylene diamine. Radical cations **7** are stabilized due to delocalization of the unpaired electron over the N=C—C=N fragment and additional conjugation through the phosphorus atom.



7

X = LEP, R = MeO, EtO;
X = O, R = Et

In the compounds with tetracoordinated phosphorus (**5** and **6**), the P—N bonds are stabilized by the electron-withdrawing >P=O group, and the transfer of spin density to the phosphorus nucleus by the mechanism of spin polarization becomes possible; this leads to a decrease in the observed HFC with the phosphorus atom, because it is partially canceled by the opposite contribution. In addition, the spin density on the >C=C< bond increases somewhat.

Table 2. Magnetic parameters of radical cations **1**—**4** and **6** and the radicals $Bu^tN^{\cdot}CH=CHN(Bu^t)P(O)(OEt)_2$ (**8**) and $Pr^iN^{\cdot}CH=CHN(Pr^i)SnPh_3$ (**9**)

Starting compound	a_P	$a_{N(1)}$	$a_{N(3)}$	$a^{Bu}_{H(1)}$	$a^{Bu}_{H(3)}$	$a^{Me}_{H(4)}$	$a^{Me}_{H(5)}$
	G						
1	56.8	3.5	3.5	3.1	3.1	8.7	8.7
2	43.5	6.7	5.0	6.5	1.3	1.5	10.0
3	57.3	3.5	3.5	3.1	3.1	8.5	8.5
4	42.0	6.7	5.0	6.5	1.3	1.5	10.0
6	8.4	3.4	3.4	2.7	2.7	9.6	9.6
8[a]	17.2	6.3	4.5	—	—	—	6.2
9[b]	23.6[c]	5.7	5.7	2.3	2.3	5.7	5.7

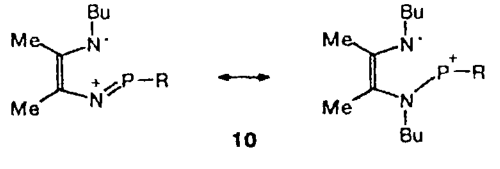
[a] See Ref. 6. [b] See Ref. 7. [c] a_{Sn}.

Electrooxidation of 2-alkyl-2,3-dihydro-1*H*-1,3,2-diazaphospholes **2** and **4** also results in the formation of paramagnetic species. The spectra exhibit a typical doublet, caused by spin-spin coupling of the unpaired electron with the phosphorus nucleus, and complex multiplets due to coupling with other nuclei in the ring. The multiplets are even, which indicates that the distribution of spin density is not symmetrical in relation to the twofold axis that passes through the phosphorus atom. The magnetic parameters calculated from the ESR spectra are listed in Table 2.

Analogous radicals arise when compound **4** is chemically oxidized by iodine in CH_2Cl_2, or in the $AlCl_3$—$MeNO_2$ system. An increase in the polarity of the medium ($CH_2Cl_2 \rightarrow MeCN \rightarrow MeNO_2$) results in a decrease in the HFC with the phosphorus nucleus. Raising the temperature causes a similar effect. These facts indirectly attest that the bond between phosphorus and the radical center is weakened. When the solution containing the radicals is frozen, the lines in the multiplets are broadened, but the doublet splitting at the phosphorus nuclei, which is not characterized by HFC anisotropy, is retained. All the foregoing, together with the fact that no HFC with the magnetic nuclei of the substituents at the phosphorus atom (Me, Et) is manifested, imply that the spin density on the phosphorus nucleus is generated *via* hyperconjugation with the radical center.

Based on the above-presented spectral data, a comparison of the magnetic parameters of compounds **2** and **4**, radical **8**, **9**, and vinylaminyl radicals, and also on the published data[8—10] on the relatively easy formation of diazaphospholes with P^{II} from dihydrodiazaphospholes with P^{III}, it can be assumed that electrooxidation of 2,3-dihydro-1*H*-diazaphospholes **2** and **4** involves the formation of radical cations **10** with a resonance structure.

It also cannot be ruled out that the asymmetry of these radical cations is due to a purely chemical factor, namely, dimerization, which is typical of compounds containing a trivalent phosphorus atom.[1]

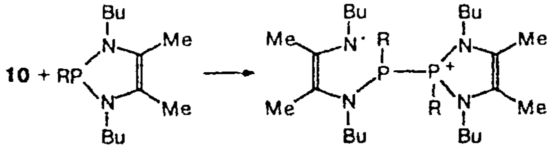


10

R = Me, Et

Oxidation of heterocyclic compounds **2** and **4** is characterized by a temperature-dependent equilibrium: the radical cations are destroyed when excess I_2 is added, and are generated again upon the addition of the initial compound.

Thus, the results obtained here indicate that 2,3-dihydro-1*H*-1,3,2-diazaphospholes are quite easily oxidized to give radical cations in which the spin density is



2, 4

mostly delocalized over the N—C=C—N fragment. The lone electron pair (LEP) of the phosphorus atom makes only a slight contribution to the highest occupied molecular orbital, but largely determines the character of the reaction products.

Electrooxidation of compound **4** in solutions, through which air had been preliminary passed, resulted in an ESR spectrum identical to that of the radical cation formed upon electrooxidation of compound **6**.

Experimental

Anodic oxidation of the title compounds, which had been obtained as described previously,[11—13] was studied by cyclic voltammetry in MeCN, purified by refluxing with $KMnO_4$ and distillation over P_2O_5, using 0.1 *M* Bu_4NBF_4 and $LiClO_4$ as the supporting electrolytes and a PI 50-1 potentiostat. A platinum disk electrode with a diameter of 0.5 mm, soldered in glass, served as the working electrode. A platinum wire served as the auxiliary electrode, and Ag/0.01 *M* $AgNO_3$ in MeCN, with a potential of +0.3 V *vs.* the SCE, served as the reference electrode. The solution was deaerated by argon. The potential sweep rate was 0.1 V s^{-1}. Tetrabutylammonium tetrafluoroborate was recrystallized from MeCN. The number of electrons was estimated by comparing the peak currents with that of the reversible one-electron oxidation peak of phenothiazine under the corresponding conditions.

The ESR spectra were recorded using an SE/X-2544 radiospectrometer. Electrooxidation was carried out directly in the resonator of the spectrometer using a cell designed at the Institute of Organic and Physical Chemistry.[14]

References

1. A. P. Tomilov, Yu. M. Kargin, and I. N. Chernykh, *Elektrokhimiya elementoorganicheskikh soedinenii. Elementy IV, V, VI grupp Periodicheskoi sistemy* [*Electrochemistry of Heteroorganic Compounds. Group IV, V, and VI Elements*], Nauka, Moscow, 1986, 296 pp. (in Russian).
2. V. V. Zverev, T. V. Gryaznova, and A. M. Kibardin, *Zh. Org. Khim.*, 1991, **61**, 2690 [*J. Org. Chem. USSR*, 1991, **61** (Engl. Transl.)].
3. A. M. Kibardin, T. V. Gryaznova, P. I. Gryaznov, and A. N. Pudovik, *Zh. Org. Khim.*, 1996, **66**, 1452 [*Russ. J. Org. Chem.*, 1996, **66** (Engl. Transl.)].
4. V. V. Zverev and V. V. Yanilkin, *Tez. dokl. Vseros. konf. po teoreticheskoi Khim.* [*All-Russian Conf. on Theoretical Chem., Abstracts*], Kazan', September 6—9, 1997, 13 (in Russian).
5. P. W. Hickmott, *Tetrahedron*, 1982, **38**, 1975.
6. A. Alberti and A. Hudson, *J. Organomet. Chem.*, 1983, **241**, 313.
7. A. Alberti and A. Hudson, *J. Organomet. Chem.*, 1983, **248**, 199.
8. A. Schmidpeter, *Phosphorus and Sulfur*, 1986, **28**, 71.
9. I. Charbonnel and J. Barrans, *C. r. Acad. Sci., C*, 1974, **278**, 355.
10. A. M. Kibardin, T. V. Gryaznova, A. N. Pudovik, and V. A. Naumov, *Zh. Org. Khim.*, 1996, **66**, 1455 [*Russ. J. Org. Chem.*, 1996, **66** (Engl. Transl.)].
11. A. M. Kibardin, Yu. B. Mikhailov, T. V. Gryaznova, and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2655 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 2461 (Engl. Transl.)].
12. A. M. Kibardin, T. V. Gryaznova, and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1676 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1554 (Engl. Transl.)].
13. A. M. Kibardin, T. V. Gryaznova, T. A. Zyablikova, Sh. K. Latypov, R. Z. Musin, and A. N. Pudovik, *Zh. Org. Khim.*, 1993, **63**, 33 [*Russ. J. Org. Chem.*, 1993, **63** (Engl. Transl.)].
14. A. V. Il'yasov, Yu. M. Kargin, and I. D. Morozova, *Spektry EPR organicheskikh ion-radikalov* [*ESR Spectra of Organic Radical Cations*], Nauka, Moscow, 1980, 168 pp. (in Russian).

Received December 19, 1997;
in revised form February 24, 1998