

# Redox Properties of Diphosphanes

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Diphosphanes undergo electrochemical one-electron oxidation. In case amino groups are at the phosphorus, the resulting distonic diphosphane radical cations disproportionate readily

into a dication and a diphosphane; the former separates into two phosphonium cations.

Recently, we have reported on the electrochemical oxidation of cyclotetraphosphanes<sup>1)</sup>, uncovering the formation of stable radical cations. Further oxidation of the intermediate radical cations yields the dication ring system which, under electrochemical conditions, undergoes rapid rearrangement to diamino phosphonium cations.

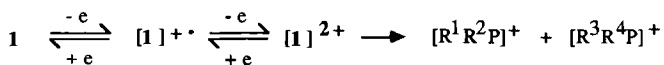
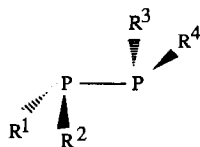
In this paper we investigate the electrochemical redox properties of a selected variety of diphosphanes. We show that these species are capable of one-electron oxidation under electrochemical conditions to radical cations, which, in a subsequent step, readily disproportionate into a dication and a diphosphane. The tendency toward disproportionation increases with increasing amino substitution at phosphorus in diphosphanes.

## Results and Discussion

### a) The Disproportionation Mechanism

The principal features of the oxidation mechanism of diphosphanes are outlined in Scheme 1.

Scheme 1



Oxidation can occur to the radical cation,  $1^{\cdot+}$ , and further to the dication,  $1^{2+}$ . The latter may not be stable and fragment readily into two phosphonium cations.

The a priori formulation of such a mechanism gets support from energy-optimized MNDO<sup>2a)</sup> and ab initio<sup>2b)</sup> calculations on a variety of model systems of substituted diphosphanes (Table 1).

The calculations reveal considerable changes in bond lengths of the neutral diphosphanes, **1**, to the corresponding dications,  $1^{2+}$ . In the parent system **1** ( $R^1 = R^2 = R^3 = R^4 = H$ ) the PP bond is shortened with increasing degree of oxidation. This is due to a

decreased repulsion of two nonbonding phosphorus lone pairs upon oxidation<sup>3)</sup>. This trend is equally well predicted at a semiempirical and ab initio level of sophistication; e.g., as compared with diphosphane (PP = 2.222 Å) the ab initio calculations predict for parent  $1^{2+}$  a considerable shortened central bond (PP = 1.968 Å). Furthermore, a vibrational analysis reveals the parent dication as an energy minimum on the electronic hypersurface. In addition, a sizable energy barrier protects  $P_2H_4^{2+}$  from fragmentation into two  $PH_2^+$  fragments. At the various ab initio levels the computed energy barriers are: SCF 26.9; 2X2 MCSCF 34.2 kcal per mole.

Table 1. Central bond lengths of model geometries, obtained from energy-optimized MNDO and ab initio calculations (in parentheses), for the parent systems, cation radicals and dications (first, second and third entry)

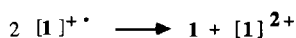
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	PP [Å]	% <sup>a)</sup>
H	H	H	H	2.023 (2.222)	0.0
				1.907	-5.7
				1.844 (1.968)	-8.8
NH <sub>2</sub>	H	H	H	2.037	0.0
				2.098	3.0
				<sup>b)</sup>	<sup>b)</sup>
NH <sub>2</sub>	NH <sub>2</sub>	H	H	2.052	0.0
				2.139	4.2
				<sup>b)</sup>	<sup>b)</sup>
NH <sub>2</sub>	NH <sub>2</sub>	NH <sub>2</sub>	H	2.084	0.0
				2.240	7.5
				<sup>b)</sup>	<sup>b)</sup>
NH <sub>2</sub>	NH <sub>2</sub>	NH <sub>2</sub>	NH <sub>2</sub>	2.095	0.0
				2.310	10.3
				<sup>b)</sup>	<sup>b)</sup>

<sup>a)</sup> Change of PP bond lengths (in percentage). — <sup>b)</sup> Fragmentation of PP bond.

An essential different picture results in case one or more substituents at phosphorus are amino groups. Then oxidation elongates the PP bond, the effect being attenuated with increasing number of amino groups at the phosphorus atoms. In other words, the tendency toward fragmentation into two phosphonium cation comes to the fore. It is already apparent in the amino-substituted radical cations.

On the basis of the computational results it seems logical to consider as further alternative the disproportionation of two intermediately formed radical cations,  $1^{+\cdot}$ , into a diphosphane, **1**, and its corresponding dication,  $1^{2+}$ , indicated as shown in Scheme 2.

Scheme 2



Having now evaluated the principal features of the oxidation mechanism of diphosphanes, we will now substantiate the model by electrochemical experiments. The cyclic voltammogram of tetrakis(diisopropylamino)diphosphane, **1a** [ $R^1 = R^2 = R^3 = R^4 = N(\text{isopropyl})_2$ ], is recorded in Figure 1.

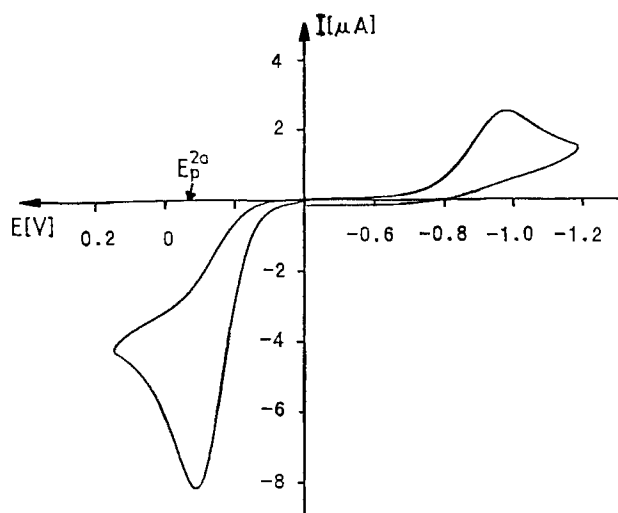


Figure 1. Cyclic voltammogram of **1a** in  $\text{CH}_2\text{Cl}_2/0.1 \text{ M TBAPF}_6$  at room temperature,  $c = 1.35 \text{ mmol/l}$ ,  $v = 100 \text{ mV/s}$

Upon electrochemical oxidation it shows an irreversibly wave at  $-0.07 \text{ V}$ . Further scan in the reductive region makes a reduction wave at  $-1.0 \text{ V}$  apparent. The latter is only obtained prior to oxidation of **1a**. Thus it originated as a decomposition product of prior oxidation. Further experimental investigations (vide infra) identify the electrochemical wave as a reduction product of an intermediately diisopropylamino phosphonium cation. Thus in accord with the results of the quantum chemical calculations **1a** decomposes upon one-electron oxidation into corresponding diamino phosphonium cations.

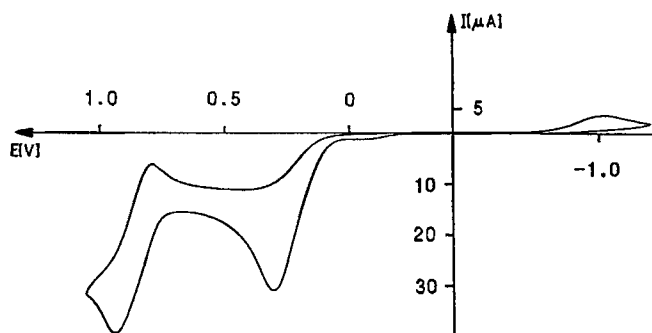
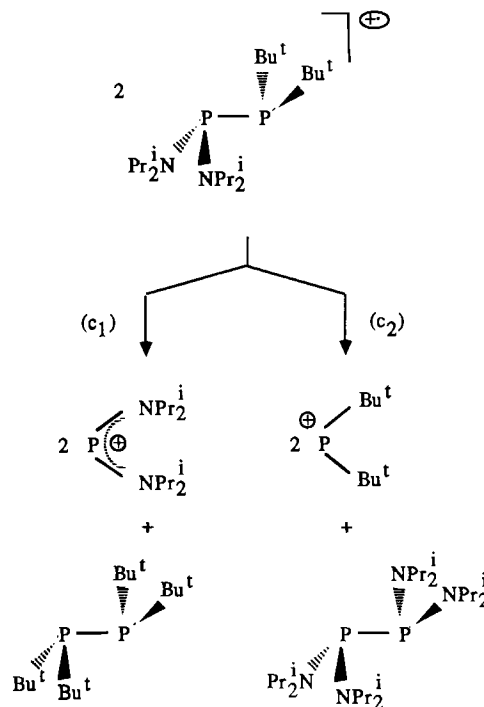


Figure 2. Cyclic voltammogram of **1b** in  $\text{CH}_2\text{Cl}_2/0.1 \text{ M TBAPF}_6$  at room temperature,  $c = 1.29 \text{ mmol/l}$ ,  $v = 100 \text{ mV/s}$

The cyclic voltammogram of 2,2-di-*tert*-butyl-1,1-bis(diisopropylamino)diphosphane, **1b**, again shows an irreversible oxidation wave at  $0.30 \text{ V}$  (Figure 2).

Further scanning reveals a second oxidation wave approximately at  $0.95 \text{ V}$ . After oxidation a wave at  $-1.0 \text{ V}$  is again obtained for reduction. Consequently, the first oxidation wave refers to one-electron oxidation with subsequent disproportionation. However, for the latter two different routes ( $c_1$ ) and ( $c_2$ ) are feasible:

Scheme 3



In route ( $c_1$ ) two diamino phosphonium cations and one tetra-*tert*-butyldiphosphane, **1d**, are formed while in route ( $c_2$ ) the amino groups reside at the diphosphane. In the electrochemical oxidation of **1b** the second oxidation wave refers to the redox reaction of an intermediately formed **1d** [route ( $c_1$ )]. For further proof we have synthesized **1d** and investigated its electrochemical properties independently. It shows an irreversible oxidation wave at  $1.10 \text{ V}$ . Furthermore, addition of a probe of **1d** to **1b** increases the second oxidation wave in Figure 2. It confirms the identification of the second oxidation wave in **1b** originating from the intermediately formed **1d**. The disproportionation mechanism according to ( $c_1$ ) is also plausible for another reason. The radical cations  $1^{+\cdot}$  are distonic<sup>4)</sup>, i.e. the radical and charge positions in these species are separated. Consequently, phosphonium cations with the largest ability for stabilization of a positive charge will separate. For completeness, the values for the four investigated diphosphanes for the first oxidation are summarized in Table 2.

Table 2. Anodic (irreversible) peak potentials for diphosphanes **1**

Compound	$R^1 (R^2)$	$R^3 (R^4)$	$E_p^{2a} [\text{V}]$
<b>1a</b>	$N(\text{iPr})_2$	$N(\text{iPr})_2$	$-0.07$
<b>1b</b>	tBu	$N(\text{iPr})_2$	$0.30$
<b>1c</b>	$\text{SiMe}_2\text{tBu}$	$N(\text{iPr})_2$	$0.45$
<b>1d</b>	tBu	tBu	$1.10$

Most difficult to oxidize is **1d**. This is in accord with the fact that alkyl groups tend to stabilize a positive charge in  $1^{+}$  or  $1^{2+}$  much less than amino groups.

#### b) Stabilization of a Phosphenium Cation

A priori, in route (c) two different disproportionation mechanism can be differentiated. This is due to the varying abilities of a substituent R to stabilize a positive charge in the corresponding phosphenium cation. A quantification of this tendency is given by the following model reaction.

Scheme 4



Corresponding reaction energies, obtained from energy-optimized MNDO calculations, are summarized in Table 3.

Table 3. Energy balance (in kcal per mole) obtained from energy-optimized MNDO calculations

R <sup>1</sup>	R <sup>2</sup>	ΔE
H	H	0.0
NH <sub>2</sub>	H	-44.4
NH <sub>2</sub>	NH <sub>2</sub>	-67.2
CH <sub>3</sub>	H	-11.0
CH <sub>3</sub>	CH <sub>3</sub>	-18.2
SiH <sub>3</sub>	H	-4.1
SiH <sub>3</sub>	SiH <sub>3</sub>	-9.4
F	F	-7.3
Cl	Cl	0.8

Negative reaction energies refer to an exothermic situation. Accordingly, amino groups are most effective in the stabilization of a positive charge at the phosphenium unit as is known from experiment<sup>3)</sup>. This supports our findings.

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## Experimental

**Materials:** Samples of the diphosphanes **1** were prepared according to literature procedure<sup>6)</sup>. In the electrochemical experiment dichloromethane (Baker Chemicals, pro analysis) was used as a solvent. It was purified by distillation over CaH<sub>2</sub> and filtration through a column of Al<sub>2</sub>O<sub>3</sub> (Riedel-de Haën, Al<sub>2</sub>O<sub>3</sub>-S, basic). As supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Fluka) was used. It was crystallized from a mixture of EtOH/H<sub>2</sub>O and dried in vacuo at 80°C over P<sub>2</sub>O<sub>5</sub>.

**Electrochemical device:** The measurements were carried out with a Princeton Applied Research (PAR) model 173 equipped with a PAR 175 universal programmer. The results were recorded on a X/Y recorder (Linseis). — For cyclic voltammetry a cell with a three-electrode configuration<sup>7)</sup> was used. The working electrode was a platinum disk electrode, the reference electrode a saturated calomel electrode (SCE). The distance between the working electrode and the tip of the Heber-Luggin capillary probe was about 1 mm to minimize the IR drop (uncompensated resistance). A platinum wire served as the counter electrode.

**Cyclic voltammetry:** All electrochemical measurements were carried out at 25°C in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBAPF<sub>6</sub> as the supporting electrolyte. Before each measurement the Pt disk was polished with alumina (0.5 μm). The solution was purged with dried argon in order to remove oxygen. The peak potentials were always reproducible to ±50 mV.

All values of electrode potentials reported here refer to the SCE. The liquid junction between the aqueous reference electrode and the dichloromethane solution was assumed to be constant and not taken into consideration<sup>8)</sup>.

Potential-controlled bulk electrolysis experiments were performed with a two-compartment cell of cylindrical symmetry; the anodic and cathodic half-cell were connected by a fine frit. A Pt-gauze cylinder was used as the working electrode, a Pt coil as the counter electrode, the reference electrode was the SCE.

For the quantitative electrolysis of **1a**, 5 mg in ca. 40 ml of CH<sub>2</sub>Cl<sub>2</sub> was electrolyzed at +0.2 V in the presence of the supporting electrolytes (either of) TBABF<sub>4</sub> (TBA tetrafluoroborate), TBAPF<sub>6</sub> or TBACl (TBA chloride). The <sup>31</sup>P-NMR spectra showed at times signals at δ = 221 and 167. Further isolation of the formed phosphenium cations was not possible, since in the presence of the supporting electrolytes further reaction occurred. This is in agreement with previous findings<sup>9)</sup>.

## CAS Registry Numbers

**1** (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H): 13445-50-6 / **1** (R<sup>1</sup> = NH<sub>2</sub>, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H): 13598-77-1 / **1** (R<sup>1</sup> = R<sup>2</sup> = NH<sub>2</sub>, R<sup>3</sup> = R<sup>4</sup> = H): 25540-10-7 / **1** (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = NH<sub>2</sub>, R<sup>4</sup> = H): 133579-01-8 / **1** (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = NH<sub>2</sub>): 63681-12-9 / **1**<sup>+</sup> (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H): 86676-97-3 / **1**<sup>+</sup> (R<sup>1</sup> = NH<sub>2</sub>, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H): 133579-02-9 / **1**<sup>+</sup> (R<sup>1</sup> = R<sup>2</sup> = NH<sub>2</sub>, R<sup>3</sup> = R<sup>4</sup> = H): 133579-03-0 / **1**<sup>+</sup> (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = NH<sub>2</sub>, R<sup>4</sup> = H): 133602-33-2 / **1**<sup>+</sup> (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = NH<sub>2</sub>): 133519-04-1 / **1**<sup>2+</sup> (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H): 133579-05-2 / **1**<sup>2+</sup> (R<sup>1</sup> = NH<sub>2</sub>, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H): 133579-06-3 / **1**<sup>2+</sup> (R<sup>1</sup> = R<sup>2</sup> = NH<sub>2</sub>, R<sup>3</sup> = R<sup>4</sup> = H): 133579-07-4 / **1**<sup>2+</sup> (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = NH<sub>2</sub>, R<sup>4</sup> = H): 133579-08-5 / **1**<sup>2+</sup> (R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = NH<sub>2</sub>): 133579-09-6 / **1a**: 128388-72-7 / **1b**: 133579-10-9 / **1c**: 133579-11-0 / **1d**: 5995-06-2 / TBAPF<sub>6</sub>: 75-09-2 / CH<sub>2</sub>Cl<sub>2</sub>: 3109-63-5

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