

Understanding phosphorus-centered radicals for a sustainably phosphor chemistry

Organo-phosphorus compounds are widely used in different fields of application from the production of pharmaceuticals to other valuable chemicals. A major problem of the use of organo-phosphorus compounds is the production of these compounds starting from the less reactive (to other reagents than oxygen) elemental form of phosphorus P_4 . All organo-phosphorus compounds nowadays are produced by the chlorination of P_4 to PCl_3 . The use of PCl_3 leads to the problem of hydrogen chloride formation, which has to be disposed. A synthetic route from P_4 to PCl_3 to organo-phosphorus compounds does not satisfy the needs of modern, sustainable and waste-free production processes. Therefore, the research of our group is aiming at the development of a PCl_3 -free synthetic route from P_4 to organo-phosphorus compounds. Oxidation reactions of P_4 involve the formation of phosphorus-centered radical cations. The understanding of these radical cations and their stabilization are necessities to achieve the goal of a direct route from P_4 to organo-phosphorus compounds.

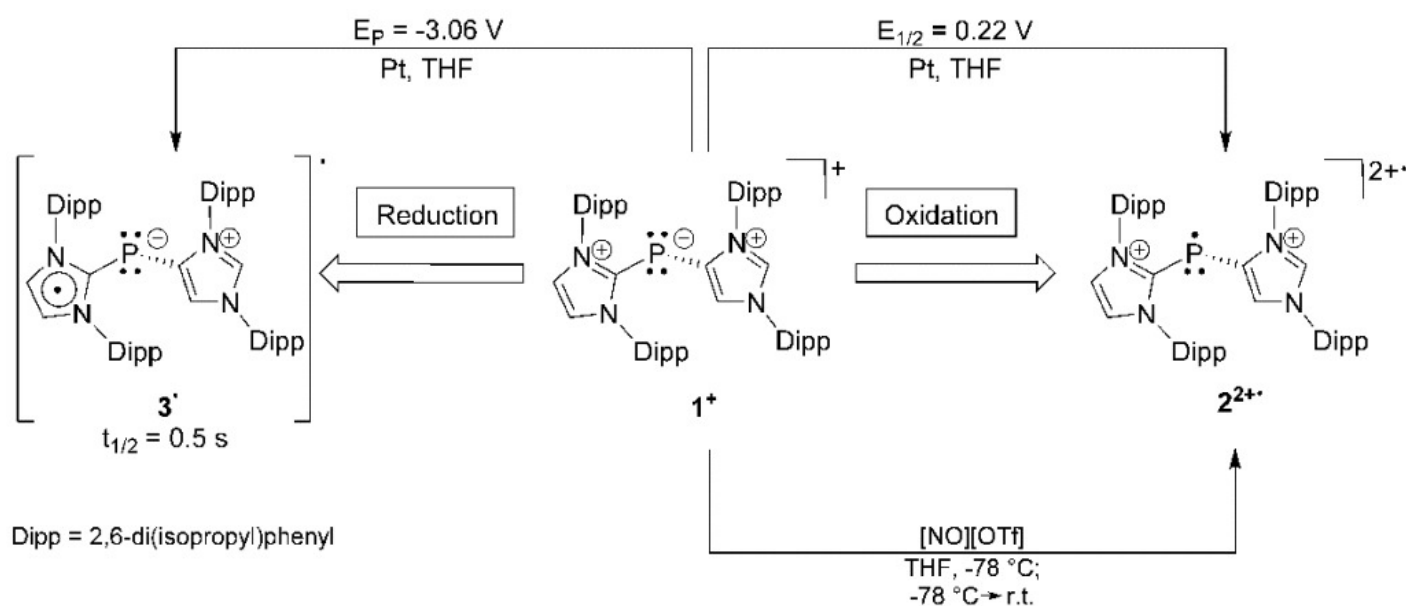


Fig. 1. Electrochemical redoxreactions and chemical oxidation of phosphorus centered cation 1^+ .

We synthesized the phosphorus-centered cation 1^+ as its triflate salt. This imidazoliumyl stabilized cation is a suitable starting material for the synthesis of the first phosphorus centered radical dication $2^{2+\cdot}$ by a one-electron oxidation reaction (Figure 1). As species with at least one unpaired electron radicals are highly reactive and tend to react with a second radical forming much less reactive dimers. This reactivity can cause unwanted side reactions in a radical involving process of

the oxidation of P_4 . In general there are two different concepts of stabilization. Thermodynamic stabilization by delocalization of the unpaired electron is one of them. Kinetic stabilization by bulky substituents is another one. In case of charged species charge repulsion plays a key role in kinetic stabilization. Therefore, a phosphorus centered radical dication $2^{2+?}$ should be stable enough to be characterized by inorganic chemical methods.

In our approach the combination of electrochemistry with UV-VIS-NIR/EPR spectroscopy was used to investigate the stability of radical dication $2^{2+?}$. Analytical electrochemical methods like cyclic voltammetry allow the oxidation of cation 1^+ to radical dication $2^{2+?}$ and the subsequent reduction back to cation 1^+ . Cyclic voltammetry generates only extremely small amounts of substances and does not provide any further information on the products of the redox reactions. However, UV-VIS-NIR spectroscopy is sensitive to changes in the electronic structure of the molecule. In combination with EPR (electron paramagnetic resonance) spectroscopy, which is sensitive to unpaired electrons, a characterization of radical intermediates is possible. The coupling of electrochemistry with UV-VIS-NIR/EPR spectroscopy as spectroelectrochemistry (SEC) combines the reaction information based on the current and the *in situ* data from the spectroscopy. Figure 2 shows the result of an UV-VIS-NIR SEC measurement from the electrode surface in reflection geometry. The visible spectra (x-axis: wavelength; z-axis: absorbance) during (y-axis: time) the sweep of the potential (right y-axis) is shown in dependence of the current (right y-axis). This measurement shows three potential cycles, in which the cation 1^+ is reversibly oxidized at $E_{1/2} = 0.22$ V (vs. $E_{1/2}(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+)$) and the *in situ* spectrum (orange curve above). A reduction at potentials lower than -3.27 V shows the formation of a neutral radical $3^?$ (green curve above). Further investigations in a transmission cuvette cell allow the prediction of the preparative accessibility of the radical dication $2^{2+?}$ and the neutral radical $3^?$.

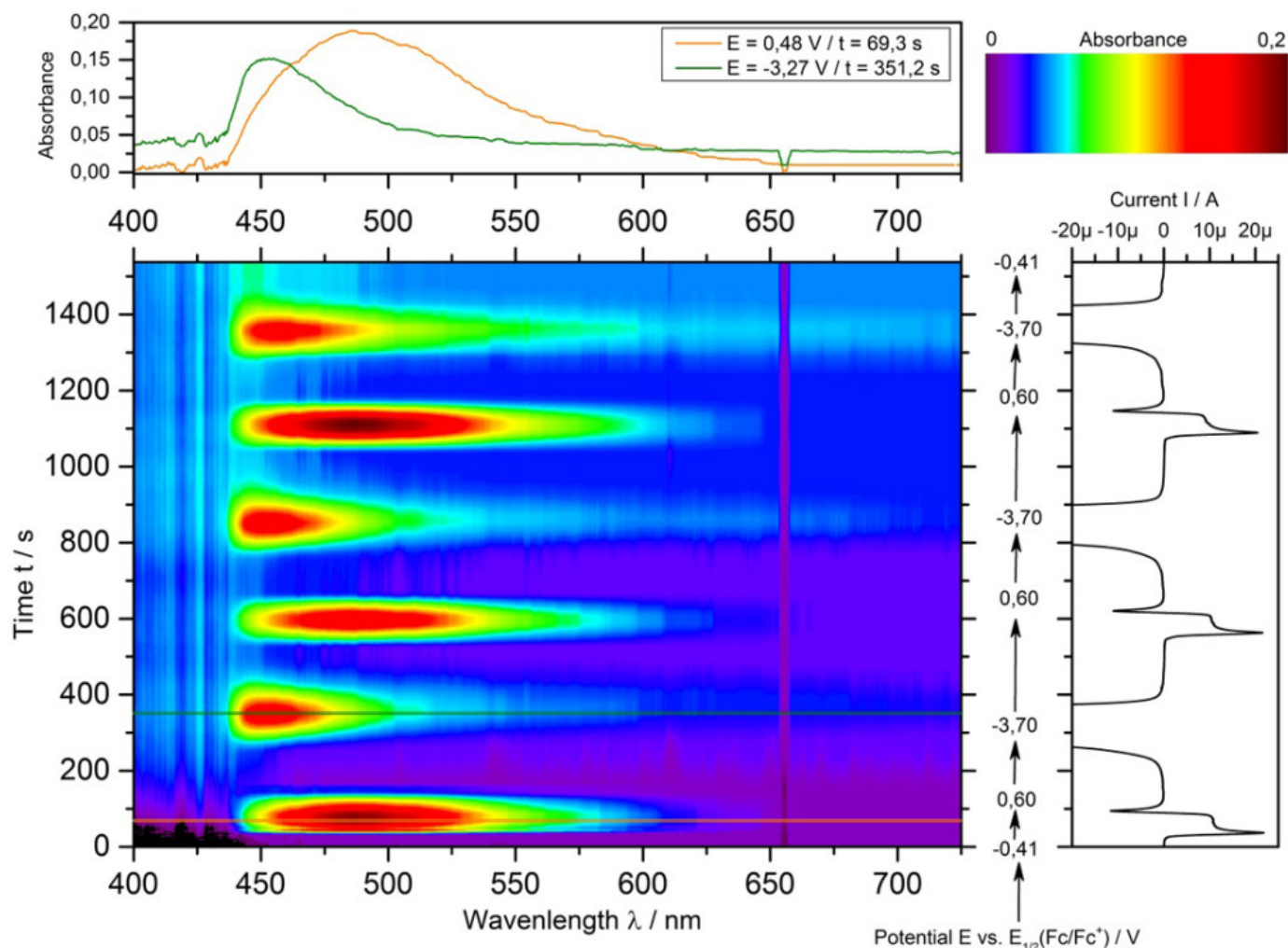


Fig. 2. In situ UV-VIS-CV 2D-Plot, VIS spectra (above), current-time curve (right) of 1[OTf] (0.0013 M) in $\text{CH}_2\text{Cl}_2/[\text{nBu}_4\text{N}][\text{OTf}]$ (0.1 M) reflection from a Pt disk (3 mm) surface at 50 mV/s.

Figure 2 shows a picture of a transmission cuvette cell during the potential sweep over the $E_{(1/2)}$ of the oxidation of 1^+ to $2^{2+?}$. The formation of the radical $2^{2+?}$ can be directly observed by a notable color change to red. This technique shows no observation of the UV-VIS-NIR spectrum of neutral radical $3^?$ because of its low stability. Combining the results from the reflective measurement and the more preparative formation in a transmission cuvette cell gives clear evidence for the high stability of radical dication $2^{2+?}$ and the low stability of neutral radical $3^{2+?}$.

Motivated by the *in situ* observation of radical dication $2^{2+?}$, subsequent preparative synthesis using nitrosyl triflate lead to the isolation of radical dication $2^{2+?}$ as a red stable solid. This highly air-sensitive material was fully characterized by means of a single crystal X-ray structure analysis. Our work showed the way from the *in situ* observation of the first phosphorus centered radical dication $2^{2+?}$ to its preparative synthesis. This proofed the concept of charge repulsion stabilization of

phosphorus radicals, which are maybe involved in a direct sustainable way from P_4 to organo-phosphorus compounds.

Publication

[Synthesis and EPR/UV/Vis-NIR Spectroelectrochemical Investigation of a Persistent Phosphanyl Radical Dication.](#)

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