

## **Dissociative attachment of low-energy electrons (below ionization or electronic excitation thresholds) in aqueous phosphate solutions**

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A related field concerns the behavior of excess electrons in liquids or solids where they can react with dissolved molecules with considerable rate constants. We review processes which are induced in phosphate monoanion  $\text{H}_2\text{PO}_4^-$  by the interaction with free electrons in an energy range typically below the ionization threshold.

The ESR spectra of the products of interaction of  $\text{H}_2\text{PO}_4^-$  with low-energy electrons the source of which were excited fluorophores  $\text{A}^*$  (the particular choice of them was to produce efficient electron injection process upon near-UV irradiation 4,0-4,5eV), were investigated in frozen aqueous dilute solutions following the scheme:  $\text{A} + h\nu \rightarrow \text{A}^* \rightarrow \text{A}^+ + e_{\text{aq}}, e_{\text{aq}} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}^\cdot + \text{HPO}_4^{2-}$  [A -ferrocyanide ions, acetate, tryptophan ( $\lambda$ -240nm), phenothiazine, 1,3,6,8-pyrenetetrasulfonic acid ( $\lambda$ -355nm)].

The photoinduced ESR spectra of solvated electron ( $g=1,9987$ ,  $\Delta H_{\text{pp}}$  0,15 G), of hydrogen atom (doublet with ~508 G separation), of secondary acceptors were suggested to be the basic indicators of the process of electron attachment to  $\text{H}_2\text{PO}_4^-$  and subsequent interaction of an electron-adduct  $[\text{H}_2\text{PO}_4^-]^\cdot$  with secondary acceptors (vanadate, flavin triplet). The reverse interrelation between ESR intensities of hydrogen atom and free electron in the experiment with acetate as fluorophore in SDS-micelle solution, interdependent ESR signal relation of hydrogen atom and donor-acceptor system, disappearance of hydrogen atom spectra after addition of electron scavenger  $\text{KNO}_3$  were observed.

This confirms the role of phosphate monoanion and its electron-adduct as acceptor-donor intermediates in models of photochemical and dark electron transport. ESR method is assumed to visualize the discharge channel of photoejected electron (or some of the form of its relaxation to  $e_{\text{aq}}$ ) to the dissociative attachment  $e^- + \text{H}_2\text{PO}_4^- \rightarrow [\text{H}_2\text{PO}_4^-]^\cdot \rightarrow \text{H}^\cdot + \text{HPO}_4^{2-}$ , which is analogous to that observed on radiolysis of Bronsted acids  $e_{\text{aq}} + \text{HX} > \text{H} + \text{X}^\cdot$ . In this context the orthophosphate is of particularly interest, because it functions in neutral pH range and in the same time is a substrate of many biochemical reactions. According to these studies, the possible range of the functional activity of phosphates can be extended to direct involvement in redox reactions.

This aspect may be of interest also for the field of study of the low-energy electrons effect on the DNA damage that results in free radical dissociation of C-O-P bond.