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Kinetics of hydrated electron reactions with phosphate anions: a laser photolysis study

P. P. Levin,★ O. N. Brzhevskaya, and O. S. Nedelina

N. M. Emanuel´ Institute of Biochemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (495) 137 4101. E-mail: levinp@sky1.chph.ras.ru

The decay kinetics of hydrated electron (e_{aq}^-) formed upon photolysis of aqueous solutions of sodium pyrene-1,3,6,8-tetrasulfonate at λ = 337 nm in the presence of phosphate anions (up to 2 mol L^{-1}) was studied by nanosecond laser-pulse photolysis in a wide range of pH (3.5—10) and ionic strength (I, up to 2 mol L^{-1}) values. At high pH values, where the HPO_4^{2-} ions dominate, the e_{aq}^- decay kinetics depends only slightly on phosphate concentration (rate constant for the reaction is at most $2 \cdot 10^5$ L mol^{-1} s^{-1}). The $H_2PO_4^-$ ions react with e_{aq}^- at a rate constant of $2.8 \cdot 10^6$ L mol^{-1} s^{-1} ($I = 0$), which increases linearly with the parameter $\exp(\sqrt{I}/(1 + \sqrt{I})$ in accordance with the Debye—Hückel theory. The rate constant for quenching of e_{aq}^- by H_3PO_4 at pH $\leq$ 4 decreases linearly with the parameter $\exp(\sqrt{I}/(1 + \sqrt{I})$ due to the secondary salt effect and equals $1.6 \cdot 10^9$ L mol^{-1} s^{-1} at $I = 0$. The logarithm of the rate constant for quenching of e_{aq}^- by phosphates is linearly related to the number of the O—H bonds in the phosphate molecule.

Key words: laser flash photolysis, hydrated electron, phosphate anions, kinetics, quenching, salt effect.

The kinetics and mechanisms of hydrated electron (e_{aq}^-) reactions with phosphate anions have been a subject of scientific research for more than four decades. The reactions can serve models in the studies of (i) mechanisms of hydrated electron interactions with phosphate-containing organic (including biologically important) substances and (ii) phosphorylation processes.[1—3] A great impetus to these investigations came from the fact of generation of H atoms in the reactions of e_{aq}^- with $H_2PO_4^-$ anions in aqueous media.[1,3,4] Earlier experiments showed that radiolysis or photolysis of water with high-energy UV radiation is accompanied by generation of H atoms as a result of the interaction of e_{aq}^- with protons of the medium or with the Brønsted acids, namely, $e_{aq}^- + HX \rightarrow HX^- \rightarrow H + X$, where HX is a protic acid.[1,4—6] In this connection, orthophosphates are of particular interest, because they are substrates of many biochemical reactions and can act as sources of H atoms at pH values similar to the physiological one (pH 7). The rate constants (k_q) for reactions of e_{aq}^- with phosphate anions and H_3PO_4 were measured using pulsed radiolysis and photolysis techniques. The rate constants, k_q, for the $H_2PO_4^-$ reactions with e_{aq}^- in aqueous media vary in the range $3.1 \cdot 10^6$—$1.9 \cdot 10^7$ L mol^{-1} s^{-1}.[3,4,7—12] The k_q value reported[9] for the reaction of HPO_4^{2-} is relatively low ($k_q = 1.4 \cdot 10^5$ L mol^{-1} s^{-1}). The fastest reaction occurs between e_{aq}^- and H_3PO_4 ($k_q = 1 \cdot 10^9$ L mol^{-1} s^{-1}).[10] Thus, successive addition of protons to the HPO_4^{2-} anion is accompanied by an increase in the k_q value by two orders of magnitude. It was assumed[4—6] that the interaction of e_{aq}^- with phosphates produces H atoms.

The generation and consumption of H atoms upon pulsed radiolysis and photolysis of aqueous solutions at λ < 200 nm can follow a number of channels involving both products of radoilytic splitting of water (particular case is the reaction between e_{aq}^- and H_3O^+ in the case of radiolysis) and transient radicals. If experiments are reduced to study the interaction between only two partners, namely, a hydrated electron emerging upon photolysis of biological cofactors (acetate, adenine, tryptophan, NADH) at $\lambda \geq$ 250 nm in the presence of a phosphate, the EPR spectra recorded in a frozen aqueous solution match those of a free electron and an H atom.[13] The EPR signal intensities correlate with the $H_2PO_4^-$ concentration in such a fashion that the stronger the EPR signal of free electron the weaker is that of the H atom.

Earlier,[3] our experiments on laser-pulse photolysis of aqueous NADH solutions at λ = 337 nm revealed that the introduction of NaH_2PO_4 into the solutions causes the lifetimes of hydrated electrons to shorten ($k_q = 1 \cdot 10^7$ L mol^{-1} s^{-1}) and the yield of e_{aq}^- to decrease. In this work we carried out a systematic nanosecond laser-pulse photolysis study of the dependences of the rate con-

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stants k_q on the pH value, phosphate concentration, and the ionic strength of the solution.

Experimental

Absorption spectra and the formation and decay kinetics of intermediate products were recorded on a nanosecond laser-pulse photolysis setup[14] using a PRA LN 1000 N_2-laser (pulse duration 1 ns, emission wavelength 337 nm) operating at a pulse repetition frequency of 10 Hz as the source of excitation. Kinetic curves were accumulated and averaged over 16—128 laser pulses using a UF.258 (Sweden) fast analog-to-digital converter connected to a personal computer based on a Pentium®IV CPU. The resolution time of the data acquisition system was 10 ns. Depending on the duration of the process under study, each kinetic curve contained from 512 to 4096 points separated by 2—4 ns time intervals. All the data reported in this work are the averaged values obtained by processing of at least ten kinetic curves obtained under the conditions mentioned above. Oxygen was removed from solutions by evacuation. The reactants used were pyrene-1,3,6,8-tetrasulfonic (PTS) acid tetrasodium salt (Eastman Kodak Chemicals), NaH_2PO_4 (Extra pure grade, Germany), and bidistilled water. The pH value was varied by adding necessary amounts of NaOH and HCl and measured with an OP-211/3 (Radelkis) pH-meter. All measurements were carried out at 20 °C.

Results and Discussion

Photoexcitation of aqueous PTS solutions ($5 \cdot 10^{-5}$ mol L^{-1}) with nanosecond laser pulses causes the formation of known intermediates including triplet PTS (^{3}PTS), $PTS^{+\bullet}$ radical cation, and a hydrated electron.[15—18] Two of them, ^{3}PTS and $PTS^{+\bullet}$, are characterized by absorption at $\lambda \le 550$ nm (relatively narrow bands with maxima at $\lambda = 430$ and 505 nm, respectively). The long-wavelength region only shows a characteristic absorption of e_{aq}^- with a broad maximum at ~700 nm. The e_{aq}^- decay kinetics obeys a monoexponential law with a rate constant ($k_{e_{aq}}$) of about $5 \cdot 10^5$ s^{-1}.

At pH ≥ 4 and no phosphate in the solution, the k_e value depends only slightly on the pH value (Fig. 1, curve *3*). In this range of pH values the hydrated electron seemingly diasppears upon addition to PTS with the formation of a $PTS^{-\bullet}$ radical anion detected from the absorption with a maximum at ~510 nm.[17—20] As the pH value decreases, the rate constant $k_{e_{aq}}$ increases due to the occurrence of the known reaction[11,21,22] of e_{aq}^- with H^+.

The introduction of NaH_2PO_4 into the solutions causes the e_{aq}^- lifetimes to shorten, the reaction rate being strongly dependent on the pH value (see Fig. 1, curves *1* and *2*). The plots of the rate constants for e_{aq}^- decay *vs.* pH value obtained in the presence of phosphate show charatceristic inflection points and correspond to the titration curves of phosphoric acid, for which $pK_a = 2.1$ and 7.2. A weak maximum at pH ~7 at relatively low phosphate concentrations (see Fig. 1, curve 2) can be due to the appearance of small amounts of peroxodiphosphate anions that interact with e_{aq}^- at rates constant higher than $1 \cdot 10^9$ L mol^{-1} s^{-1}.[23]

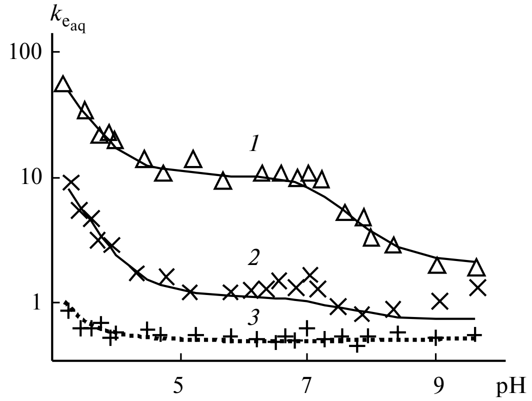

Fig. 1. Rate constant for e_{aq}^- decay ($k_{e_{aq}}$) plotted *vs.* pH value at a NaH_2PO_4 concentration of 1 (*1*), 0.1 (*2*), and 0 mol L^{-1} (*3*).

At pH 9.6, the plot of the rate constant for e_{aq}^- decay *vs.* phosphate concentration (phosphate is present in the solution in the form of HPO_4^{2-} anions) is a curve with saturation (Fig. 2). A similar dependence of $k_{e_{aq}}$ on the salt concentration, which is observed upon introduction of NaCl instead of phosphate into the solutions, indicates that such a behavior is due to the effect of the ionic strength (*I*) of the solution on the rate of the reaction between e_{aq}^- and PTS that bears four negative charges. The rate constant for the reaction of e_{aq}^- with HPO_4^{2-} estimated from the difference between the $k_{e_{aq}}$ values measured at high concentrations of NaH_2PO_4 and NaCl is at most $2 \cdot 10^5$ L mol^{-1} s^{-1}, being consistent with the published data.[9,10]

Figure 3, *a* shows the rate constant for e_{aq}^- decay plotted *vs.* phosphate concentration at $5 \le pH \le 6$ (phosphate is present in the solution in the form of $H_2PO_4^-$ anions). The nonlinear shape of the curve is due to the effect of the ionic strength of the solution on the rate of the reaction between the two negatively charged species.

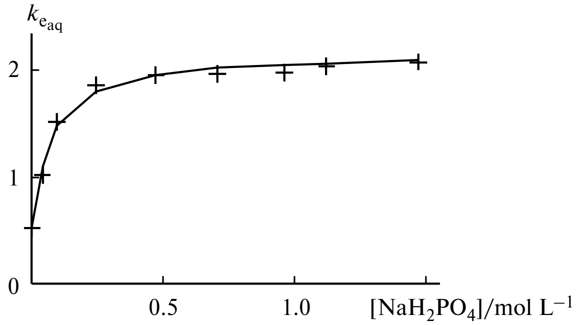

Fig. 2. Rate constant for e_{aq}^- decay ($k_{e_{aq}}$) plotted *vs.* NaH_2PO_4 concentration at pH 9.6.

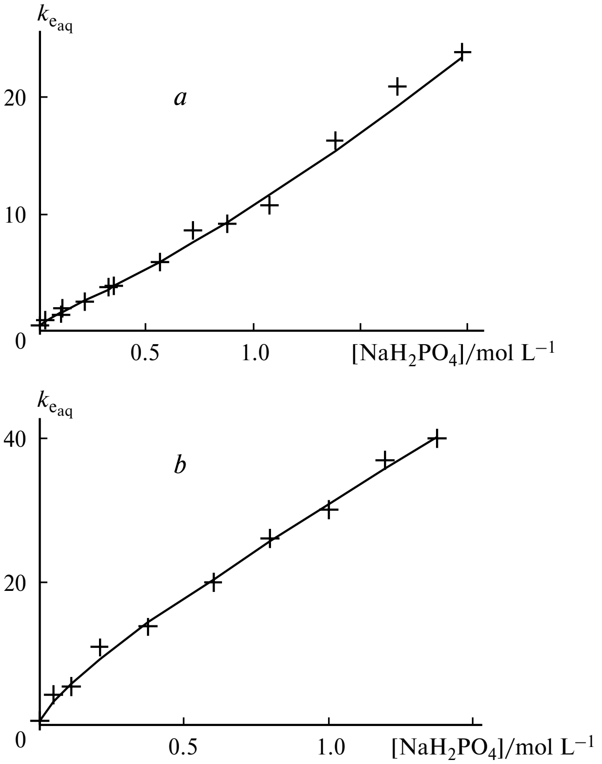

Fig. 3. Rate constant for e_{aq}^- decay ($k_{e_{aq}}$) plotted *vs.* NaH_2PO_4 concentration at a pH value of 5.3 (*a*) and 3.5 (*b*). The solid curve denotes the results of calculations using Eq. (1).

A similar experiment in a NaCl solution at [NaCl] + $[NaH_2PO_4]$ = 1 mol L^{-1} gave a linear dependence of $k_{e_{aq}}$ on the phosphate concentration. The plot in Fig. 3 is satisfactorily described in the framework of the Debye—Hückel theory of electrolyte solutions

$$k_{e_{aq}} - k_0^{\mathrm{corr}} = k_q^0[NaH_2PO_4]\exp[Z_aZ_b\sqrt{I}/(1 + \sqrt{I})\log10], \quad (1)$$

where k_0^{corr} is the rate constant for the e_{aq}^- decay in the absence of phosphate with allowance for the effect of the ionic strength of the solution, k_q^0 is the rate constant for quenching of e_{aq}^- by phosphate at $I = 0$, and Z_a and Z_b are the charges of the interacting ions. The k_q^0 value thus obtained equals $2.8 \cdot 10^6$ L mol^{-1} s^{-1}, which is lower than the values obtained in the solutions with the nonzero ionic strength.[3—12]

At pH ≤ 5, the decrease in the pH values of the phosphate solutions is accompanied by an increase in $k_{e_{aq}}$ (see Fig. 1) due to the efficient reaction with H_3PO_4.[10] The rate constant for the e_{aq}^- decay is plotted *vs.* phosphate concentration at pH 3.5 in Fig. 4. The nonlinear shape of the curve can be due to the effect of the ionic strength of the solution on the rate of the reaction between two unlikely charged species and on the dissociation constant of phosphoric acid (secondary salt effect). The latter seems to be more probable. In this case the concentration dependence can also be described by expression (1). The k_q^0 obtained for the reaction of e_{aq}^- with H_3PO_4 with allowance for the contribution of the interaction with $H_2PO_4^-$ at pK_a (H_3PO_4) = 2.12 and $I = 0$ equals $1.6 \cdot 10^9$ L mol^{-1} s^{-1}.

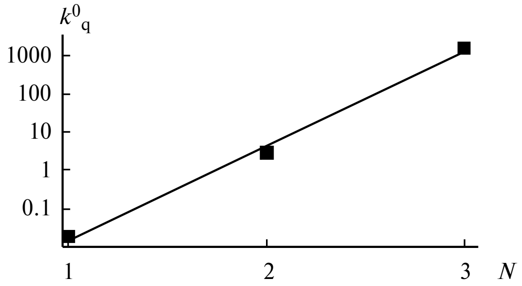

Fig. 4. Rate constant (k^0_q) for quenching of e_{aq}^- by phosphates at zero ionic strength plotted *vs.* number of O—H bonds in the phosphate molecule.

Thus, an increase in the number of highly polarized O—H bonds in the phosphate molecule is accompanied by abrupt increase in the rate constant for the reaction of phosphate with hydrated electron. Assuming that the reaction of e_{aq}^- with HPO_4^{2-} is characterized by k_q^0 = $1.8 \cdot 10^4$ L mol^{-1} s^{-1} (obtained by extrapolating the value $k_q = 1.4 \cdot 10^5$ L mol^{-1} s^{-1} measured[7] at $I = 0.6$ to $I = 0$ using expression (1)), one can obtain a nearly logarithmic dependence of k_q^0 on the number, N, of O—H bonds in the phosphate molecule (see Fig. 4, $k_q^0 = 49\exp(5.7N)$ L mol^{-1} s^{-1}).

Summing up, the observed capture of electron by orthophosphate in aqueous medium under physiological conditions is consistent with the modern concepts of the formation of short-lived electron adducts of biomolecules (metastable anions, resonants) that deliver electrons to the reaction zone.[24] The formation of such species was experimentally proved in resonance electron capture mass spectrometry studies of many compounds including nucleotides[25,26] and amino acids.[27] This concept is widely used in the rapidly progressing field of research on the effect of low-energy electrons on DNA and nucleotides that causes free-radical induced bond dissociation in the C—O—P fragment.[28] Earlier, the nature of the primary product of the reaction between electron and phosphate in frozen aqueous solution was treated in some different fashion, namely, it was assumed to be a $H_2PO_4^{2-}$ diradical anion in which the extra electron is localized on the δ*-bond O—H, which is detected as a hydrogen atom by EPR spectroscopy.[29]

Photochemical experimental studies on the interaction of low-energy electrons with biological substrates can serve an excellent model for investigations of the mechanisms of reductive splitting of chemical bonds upon radiation-induced damage.[30]

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