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Picosecond Pulse Radiolysis of Highly Concentrated Phosphoric Acid Solutions: Mechanism of Phosphate Radical Formation

Jun Ma, Uli Schmidhammer, and Mehran Mostafavi*

Laboratoire de Chimie Physique, CNRS/Université Paris-Sud, Bât. 349, 91405 Orsay, France

ABSTRACT: Eight solutions containing phosphoric acid with concentrations ranging from 2 mol L^{-1} to neat acid have been studied by picosecond pulse radiolysis. The absorbance of the secondary radical $H_2PO_4^\bullet$ formed within 7 ps of the electron pulse is observed using pulse−probe method in the visible. Kinetic analysis shows that the radicals of phosphoric acid are formed via two mechanisms: direct electron detachment and oxidation by the radical cation of water, $H_2O^{\bullet+}$. On the basis of molar extinction coefficient value of 1850 L mol^{-1} cm^{-1}, at 15 ps the radiolytic yield of $H_2PO_4^\bullet$ formation by direct energy absorption is $3.7 \pm 0.1 \times 10^{-7}$ mol J^{-1} in neat phosphoric acid. In highly concentrated phosphoric acid solutions, the total yield of phosphate radical at 15 ps exhibits an additional contribution that can be explained by electron transfer from phosphoric acid to $H_2O^{\bullet+}$. The efficiency of the electron transfer to this strongly oxidizing species in phosphoric acid solutions is lower compared with the one in sulfuric acid solutions. Two explanations are given to account for a relatively low efficiency of $H_2O^{\bullet+}$ scavenging in concentrated phosphoric acid solutions.
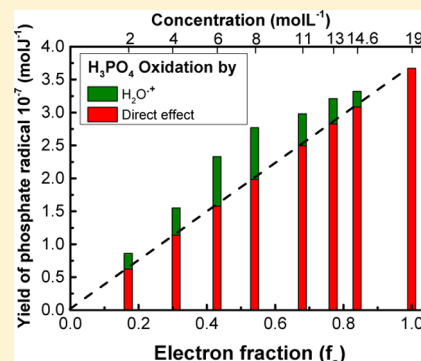
INTRODUCTION

The interaction of energetic particles with water results in the excitation and ionization of water molecules. The ionization process (R1 in Table 1) refers to the generation of the excess electrons detached from their parent molecules and leaving behind the positive hole (denoted $H_2O^{\bullet+}$). Together with the excited water molecule H_2O^{**}, these highly reactive species localized over several solvent molecules trigger the subsequent chemical reactions in radiolytic spurs. Among these reactions, the proton transfer between $H_2O^{\bullet+}$ and the neighboring water molecule that yields OH$^\bullet$ radical and H_3O^+ (R2 in Table 1) is believed to complete in less than a few tens of femtoseconds, which is even faster than the hydration of the excess electron. However, when the local hydration structure is modified by other molecules, as is the case in concentrated solutions, the direct effect of radiation on the solute should be considered and the pattern of spur reactions becomes completely different from that in dilute aqueous solutions.[1]

Our recent studies on concentrated aqueous solution of acids indicate that the following three mechanisms of oxidation can occur in such systems: (i) The direct effect of radiation on the solute detaching an electron from this solute; (ii) the oxidation by $H_2O^{\bullet+}$, when the solute is in contact with this radical; and (iii) the oxidation of the solute by OH$^\bullet$ radical. In our previous studies of concentrated Cl$^-$, Br$^-$, and NO$_3^-$ solutions, it was demonstrated that the contribution of $H_2O^{\bullet+}$ radical in the oxidation mechanism can be quantified when the rate constant of the reaction between the solute and OH$^\bullet$ radical is sufficiently low. For sulfuric acid, it was possible to estimate the yield of radical formation in the picosecond range through oxidation by water hole through measuring directly the yield of sulfate radical in neat sulfuric acid. For these systems, it was shown that the electron transfer reaction between the water hole and

the solute could be more rapid than a proton transfer reaction involving this hole as the number of water molecules in proximity decreases.[2−8]

In the present work, a picosecond pulse radiolysis study of phosphoric acid has been carried out in order to further examine the reactivity of $H_2O^{\bullet+}$. The study is motivated by several considerations: First, the oxidation of phosphoric acid by OH$^\bullet$ is more difficult than that of sulfuric acid. The rate constant of the reaction between OH$^\bullet$ and the phosphoric acid is low.[9] Second, the phosphate group ubiquitously occurs in biosystems. For example, if a biomolecule such as DNA is under the exposure to ionizing radiation, the sugar−phosphate backbone can be damaged either by direct detachment or by indirect oxidation from the water radicals and the phosphate-centered radicals are expected to be formed in appreciable yields, leading to subsequent biological effects.[10,11] Phosphate radical reacts with numerous organic or inorganic compounds by abstraction or addition and also by electron transfer. It is therefore important to estimate the yield of damage through the direct radiation effect and through oxidation by $H_2O^{\bullet+}$.[12−16] For this reason, highly concentrated H_3PO_4 matching the fraction of phosphate in DNA can be used as a simple model system to study oxidation of the phosphate compound of DNA and to evaluate the probability for the positive holes to oxidize H_3PO_4 and solute ions (R5).

Previously, several studies have been carried out on pulse radiolysis and flash photolysis of phosphoric acid and phosphate

Table 1. Primary Reactions Involved in Pulse Radiolysis of Aqueous Solutions of Concentrated Phosphoric Acid

reactions	
$H_2O \rightarrow H_2O^{\bullet+} + e^-$	(R1)
$H_2O + H_2O^{\bullet+} \rightarrow H_3O^+ + OH^\bullet$	(R2)
$H_3PO_4 \rightarrow H_2PO_4^\bullet + e^- + H^+$	(R3)
$OH^\bullet + H_3PO_4 \rightarrow H_2PO_4^\bullet + H_2O$	(R4)
$H_2O^{\bullet+} + H_3PO_4 \rightarrow H_2PO_4^\bullet + H_3O^+$	(R5)
$H_3O^+ + e^- \rightarrow H_2O + H^\bullet$	(R6)
$H_2O^{\bullet+} + e^- \rightarrow H_2O$	(R7)
$H_3PO_4 \text{ (s)} + H_2O \rightleftarrows H_2PO_4^- \text{ (aq)} + H_3O^+ \text{ (aq)} \quad pKa1 = 2.12$	(R8)
$H_2PO_4^- \text{ (aq)} + H_2O \rightleftarrows HPO_4^{2-} \text{ (aq)} + H_3O^+ \text{ (aq)} \quad pKa2 = 7.21$	(R9)
$HPO_4^{2-} \text{ (aq)} + H_2O \rightleftarrows PO_4^{3-} + H_3O^+ \text{ (aq)} \quad pKa3 = 12.67$	(R10)
$H_2PO_4^- \text{ (aq)} + H_3PO_4 \text{ (aq)} \rightleftarrows H_5P_2O_8^- \text{ (aq)}$	(R11)

Table 2. Concentration of Phosphoric Acid Solutions and Relevant Parameters[a]

C [mol L^{-1}]	f_s	f_w	F (g/cm^3)	d_{sol} (g/cm^3)	[H$_2$O]/[H$_3$PO$_4$]	$A_{H_2PO_4^\bullet} \times 10^3$ (t = 15 ps)	$G_{H_2PO_4^\bullet}$ 15 ps $\times 10^7$ mol J^{-1}
2	0.17	0.73	1.09	1.11	25.3	1.76	0.86
4	0.31	0.69	1.17	1.20	11.2	3.16	1.55
6	0.43	0.57	1.24	1.29	6.5	4.75	2.33
8	0.54	0.46	1.33	1.39	4.2	5.65	2.77
11	0.68	0.32	1.45	1.55	2.4	6.08	2.98
13	0.77	0.23	1.51	1.62	1.46	6.56	3.21
14.6	0.84	0.16	1.57	1.68	0.96	6.77	3.32
Neat	1	0	1.73	1.88	0	7.49	3.67

[a]Electron density fraction of solute f_s, electron density fraction of water f_w, dose factor F, and solution density d_{sol}. The absorbance of $H_2PO_4^\bullet$ at 15 ps is obtained from $A_{H_2PO_4^\bullet}$ (t = 15 ps, λ = 520 nm) = A_{obs}(t = 15 ps, λ = 520 nm) − $A_{solvated\ electron}$(t = 15 ps, λ = 520 nm) − A_{cell} (t = 15 ps, λ = 520 nm). The value of the absorbance due to the transient species induced in the windows of the cell around 520 nm, A_{cell} (15 ps) is 6.11 ×10^{-4} based on the work reported in ref 23.

anions.[17−21] The radical $H_2PO_4^\bullet$ has been identified as the main intermediate in radiolysis of H_3PO_4 aqueous solutions; this radical has an absorption band with a maximum around 520 nm using nanosecond pulse radiolysis.[9,17−19] It was found that the G value of direct electron detachment on H_3PO_4 (R3) is 3.4×10^{-7} mol J^{-1}.[9] The rate constant for the reaction between $OH^\bullet$ radical and H_3PO_4 was determined (R4) by varying the concentration of the phosphate. It was shown that the rate constant of this reaction is 4.2×10^4 mol^{-1} L s^{-1}, which is quite low.[9]

Highly concentrated H_3PO_4 solutions and even transparent neat H_3PO_4 in liquid state can be obtained at the room temperature. In the present work, several highly concentrated phosphoric acid solutions have been studied using picosecond pulse radiolysis. The mechanism for phosphate group oxidation is discussed and the yield of the formation of the phosphate radical is deduced from the transient absorption observed in these solutions. The yield of oxidation at picosecond range is compared with the one in highly concentrated sulfuric acid solutions.

■ EXPERIMENTAL SECTION

The picosecond pulse radiolysis measurements were performed at ELYSE facility, which is a picosecond electron accelerator based on the radiofrequency photogun technology.[22] The transient absorption pulse−probe setup uses time synchronization resulting from the laser triggered Cs$_2$Te photocathode. The main part of a femtosecond Ti:sapphire laser output is

frequency tripled and used to produce the electron pulse that is accelerated by the RF fields. A fraction of the laser output is split off to generate an optical probe pulse that is delayed relative to the electron pulse using a delay stage. As described in ref 23, multiple probe wavelengths can be generated and detected using a multichannel detection system that is placed in the focal plane of a polychromator. The kinetics of several transient species absorbing at different wavelengths is acquired simultaneously. A visible light supercontinuum in CaF$_2$ generated, observe the transient absorption spectra over the entire visible region.

These optical measurements were carried out in a fused silica optical flow cell with a 5 mm optical path in solution, the probe beam was collinear with the electron pulse propagation. The electron pulses had a charge of 4 nC and a duration <10 ps, the mean electron energy was 6−8 MeV. More experimental detail can be found in ref 23. Here we used a custom-made glass cell with reduced thickness (200 μm) for the entrance and exit windows. In this configuration, transient absorbance in this cell immediately after the pulse is <1 mOD in the visible range (the absorbance maximum is at 600 nm) for a dose of 22.1 J kg^{-1} per pulse.

After subtraction of the remaining contribution from the cell windows, the transient absorption observed in water measured in the visible and near-infrared is due to the hydrated electron; this absorbance is used as a reference for dosimetry assuming radiolytic yield $G(e_{hyd}^-) = 4.25 \times 10^{-7}$ mol J^{-1} at 10 ps.[24] The energy deposited in concentrated acidic solutions D_{sol} is

increased relative to neat water by direct radiolysis of the solutes. The effective dose considering this contribution can be derived from the reference dose in pure water D_{water} as follows

$$D_{sol} \; (J \; L^{-1}) = F D_{water} \; (J \; kg^{-1}) \tag{1}$$

with

$$F = d_{sol} \left(\frac{Z_{PO_4^{3-}} p}{A_{PO_4^{3-}}} + \frac{Z_{water}(100 - p)}{A_{water}} \right) \left(\frac{Z_{water} 100}{A_{water}} \right)^{-1} \tag{2}$$

where d_{sol} is the density of the solution, Z is the number of electrons, A is the mass number, and p is the weight fraction of the solute percent. The estimate F and other relevant properties for aqueous solutions of phosphoric acid are given in Table 2.

The phosphoric acid was obtained from Sigma-Aldrich. The measurements were performed at 22.5 °C. At this temperature, neat phosphoric acid is solid. By heating to 50 °C, this solid melts becoming liquid and then it remains a supercooled liquid for several days at an ambient temperature. Therefore, pulse radiolysis measurements on this neat supercooled phosphoric acid were possible.

■ RESULTS

Transient absorption spectra of phosphoric acid aqueous solutions ($2-19$ mol L^{-1} obtained at the time delay of 15 ps) are presented in Figure 1. The species that exhibits a broad and
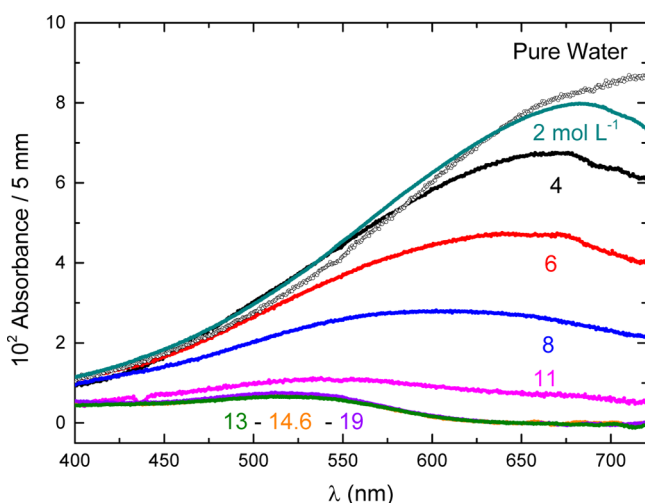
Figure 1. Transient absorption spectra obtained 15 ps after the picosecond electron pulse in $2-19$ mol L^{-1} H_3PO_4. The contribution of transient absorption induced in the cell windows has been subtracted. The radiation dose deposited in neat water is 22.1 Gy.

featureless band across the visible and near-IR is the transient pair of the solvated electron and hydronium cation (H_3O^+) as discussed in ref 25. Of great interest for the present study is another absorption band that is located in the UV−visible, which becomes more prominent as the solvated electron is scavenged by H_3O^+ ions in these acidic solutions. For the solutions containing >11 mol L^{-1} phosphoric acid, the absorbance due to the hydrated electron decays within the electron pulse (7 ps). The remaining absorbance is from a species that is formed within the duration of the electron pulse. In order to identify this intermediate, the contribution of the hydrated electron is subtracted and the difference spectra are presented in Figure 2. A feature in these resulting absorption spectra that exhibits a maximum at 520 nm is
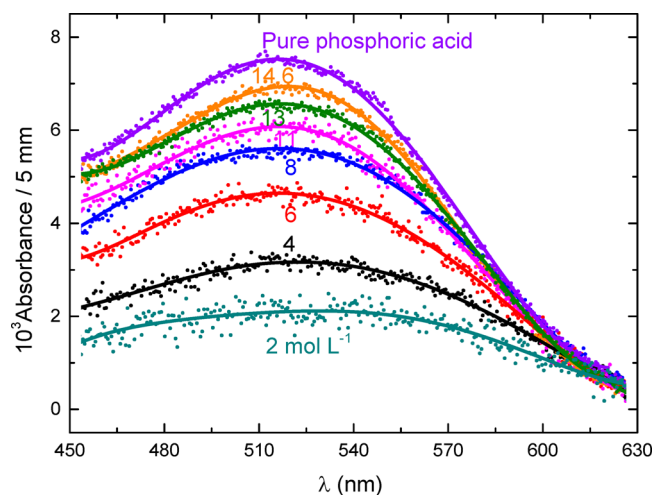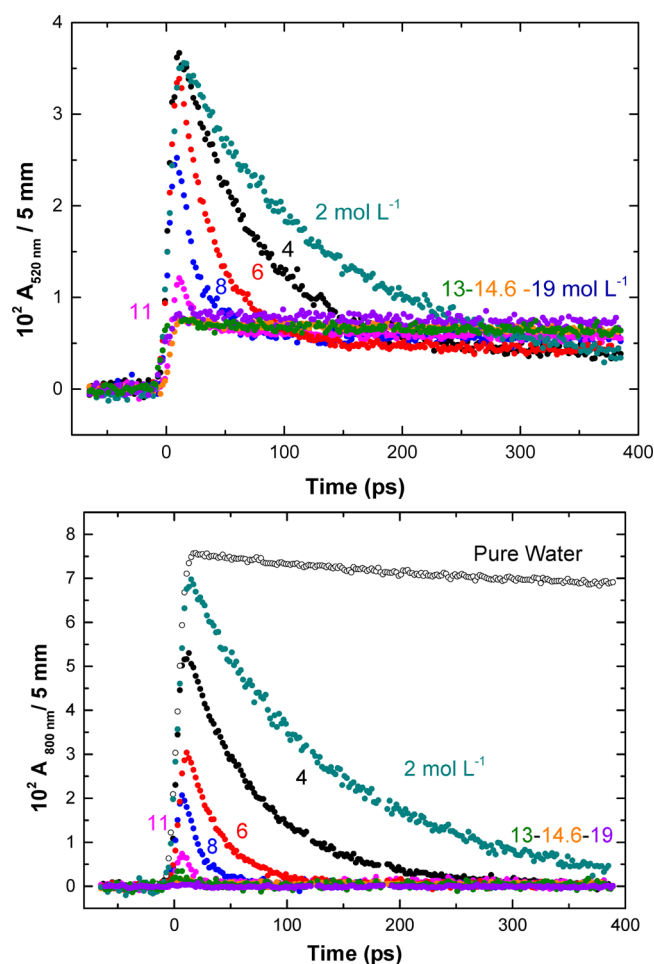

Figure 2. Transient absorption spectra of the radical ($H_2PO_4^{\bullet}$) observed at $t = 15$ ps in $2-19$ mol L^{-1} H_3PO_4. The contribution of solvated electron in $2-11$ mol L^{-1} H_3PO_4 was subtracted from the signal.

attributed to the protonated form of the phosphate radical ($H_2PO_4^{\bullet}$), which is in good agreement with several previous observations using photolysis and radiolysis on the microsecond time scale.[9,17−19,21] In radiolysis of sulfuric acid, the spectrum of the sulfate radical ($HSO_4^{\bullet}$) undergoes red shift in $12-18$ mol L^{-1} solutions due to the protonation of the radical, while the spectra of the phosphate radical are concentration independent in $2-19$ mol L^{-1} solutions, as shown in Figure 2. The reason is that the reported pK_a (5.7) of $H_2PO_4^{\bullet}$ is much greater than that of ($HSO_4^{\bullet}$) so the phosphate radical stays protonated even in more dilute solutions.[9,26]

Figure 3b shows decay kinetics of the hydrated electron in phosphoric acid solutions of different concentrations observed at 800 nm (Figure 3b). This decay becomes faster with increasing concentration of H_3PO_4 leading to a complete decay of the absorbance on the picosecond time scale. It is known that the decay of the transient pair $(e_s^-, H_3O^+)_{hyd}$ involves the hydronium cation so the increase of H_3O^+ concentration due to the dissociation of H_3PO_4 in water accelerates the decay. Moreover, the initial transient absorption at 800 nm substantially decreases as the rapid reaction of presolvated electron with H_3O^+ (R6 in Table 1) occurs in concentrated solutions.[25] The kinetic behavior at 520 nm differs considerably from the one observed at 800 nm.[25] The rapid decay is followed by a plateau after a certain delay time that varies with the acid concentration (Figure 3a). In fact, both the (paired) solvated electron and $H_2PO_4^{\bullet}$ absorb at this wavelength in dilute solutions; the rapid decay component is apparently due to the solvated electron. In concentrated acid solutions ($11-19$ mol L^{-1}), the scavenging of the electron is completed within the electron pulse, and the slow decay corresponds to the kinetics of $H_2PO_4^{\bullet}$. The initial absorption increases as the concentration of phosphoric acid increases (Figure 4).

Special attention has been paid to radiolysis of pure phosphoric acid, which enabled us to determine the direct radiolytic yield, G_{dir}, of $H_2PO_4^{\bullet}$. As the same absorption spectra is observed in neat acid, it can be considered that in neat phosphoric acid, the electron detachment is followed by deprotonation, which is very rapid; consequently only $H_2PO_4^{\bullet}$ is formed within the duration of the electron pulse. The molar extinction coefficient of $H_2PO_4^{\bullet}$ was estimated as 1850 L mol^{-1} cm^{-1} in this study, which is in agreement with the value reported in the

Figure 5. Radiolytic yield of phosphoric acid radical versus the electron fraction of the solute. The obtained yield at 19 mol L^{-1} is considered as the direct effect yield that is linearly extrapolated to the zero (dash line). The superliner contribution (green bars) is due to the charge transfer reaction involving water radical cation H$_2$O$^{•+}$.
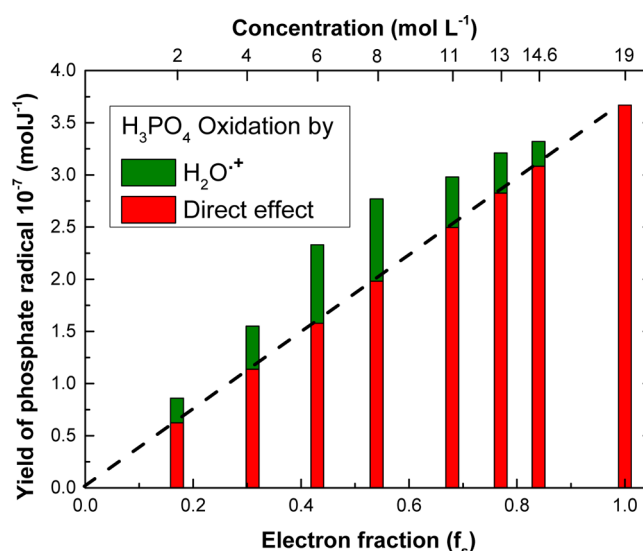
Figure 3. (a) Decay of absorbance for solutions containing H$_3$PO$_4$. The concentrations are given in the plot. (b) Decay of absorbance for solutions containing H$_3$PO$_4$. In (a,b) The transient absorbance in this plot was divided by the factor F to take into account the direct radiolysis (see text).
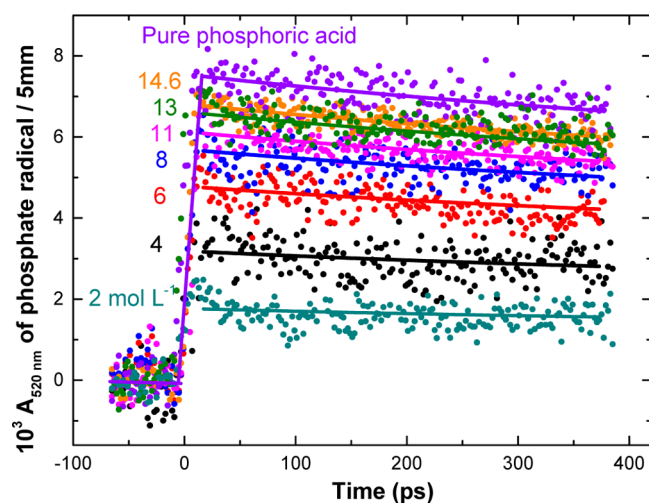
Figure 4. Kinetics of the (H$_2$PO$_4^•$) radical in aqueous H$_3$PO$_4$. The contribution of solvated electron in 2−11 mol L^{-1} H$_3$PO$_4$ has been subtracted as described in the text. The nominal concentrations of the phosphoric acid are indicated in the plot.

literature.[9] The yield of H$_2$PO$_4^•$ observed as a function of the electron density fraction is shown in Figure 5. The direct effect is proportional to the electron density fraction that was estimated from the radiolytic yields in the neat phosphoric acid. As the oxidation of H$_3$PO$_4$ by OH$^•$ radical is too slow to occur on the picosecond time scale, the supplementary yield, G_{indir}, observed for each concentration is considered due to the scavenging of H$_2$O$^{•+}$ by rapid electron transfer reaction (R5).

The observed yield, G_{exp}, after the electron pulse obeys eq 3

$$G_{exp} = f_s G_{dir} + f_w G_{indir} \qquad (3)$$

We have demonstrated that in the sulfuric acid system the electron transfer from the solute to H$_2$O$^{•+}$ competes with proton transfer reaction (R2) as the solute disturbs water molecules in the solvation shell. This reaction is the predominate reaction that involves H$_2$O$^{•+}$ and it also competes with the geminate recombination of the H$_2$O$^{•+}$ and the excess electron (R7).

It is important to note that in the acidic solutions, H$^•$ atom could also participate in the oxidation mechanism forming the phosphate radical. However, this reaction is not considered because the yield measurements are performed at 15 ps, which is too short to observe radical formation through H$^•$ atom reactions.

In Figure 6, the yield of H$_2$O$^{•+}$ scavenging in phosphoric acid is compared with sulfuric acid. The value of the yield increases as the concentration increases to 6 mol L^{-1} reaching a constant level of 1.5 mol J^{-1}. For scavenging of H$_2$O$^{•+}$ by phosphoric acid, this plateau value is lower than for sulfuric acid. In the latter case, the yield of scavenged H$_2$O$^{•+}$ increases up to 12 mol L^{-1} reaching a constant level of 5.2 mol J^{-1}. Therefore, it appears that the charge transfer in the phosphoric acid system is less efficient than in the sulfuric acid system.

Knowledge of thermodynamics and chemical composition for H$_3$PO$_4$ solutions is essential for understanding chemical reactions in this system. Phosphoric acid exhibits dissociation constants that increase 5 pK units in each consecutive dissociation step (Table 1). In dilute solutions, all protons can dissociate and interact with water molecules by forming H bonds, leaving the anion behind. At high concentration of the acid, as the second and third dissociation constant decrease, the further dissociation
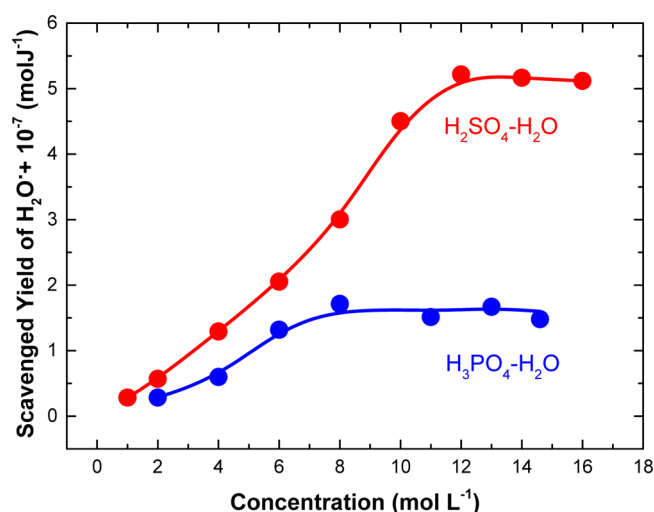
Figure 6. End of pulse radiolytic yield of scavenged radical cation $H_2O^{\bullet+}$ in aqueous sulfuric and phosphoric acid solutions.

can be disregarded. The established speciation model indicates that $(H_2PO_4^-)$ anions further interact with undissociated acid yielding $(H_5P_2O_8^-)$ anions by forming an H bond (R11). Therefore, the main species in phosphoric acid solution over the concentrations range below 14.6 mol L^{-1} are H^+, $H_2PO_4^-$, H_3PO_4, and $H_5P_2O_8^-$. Other dimer species involving $H_6P_2O_8$, $H_4P_2O_8^-$, and $H_3P_2O_8^{3-}$ are omitted from our consideration as they are less stable and their concentration is low.[27] The formation of dimers at high concentration changes the ratio between the number of water molecules interacting with the solute, decreasing the probability that a phosphoric species is in contact with a water molecule.[28,29] We believe that the radical cation of water, $H_2O^{\bullet+}$, can be involved in a charge transfer reaction provided that it forms a contact with the charge acceptor. For concentrated phosphoric acid, due to dimer formation the concentration of H_3PO_4 is almost two times lower than the nominal concentration of the phosphoric acid. For example, at 10 mol L^{-1} the species H_3PO_4, $H_2PO_4^-$, $H_5P_2O_8^-$ and $H_4P_2O_8^{2-}$ are present at concentrations of 0.64, 0.06, 3.7, and 0.9 mol L^{-1}, respectively. Consequently, $H_2O^{\bullet+}$ cannot efficiently react with some of these species. In contrast, such dimers have not been reported for sulfuric acid. This can explain why the hole scavenging efficiency in phosphoric acid solutions is lower than in sulfuric acid solutions. Moreover, for a given concentration in phosphoric acid solutions the concentration of free H_3O^+ is lower than in sulfuric acid solutions. For the same solution of 10 mol L^{-1}, the concentration of free H_3O^+ is estimated to be 10 and 3.8 mol L^{-1} in sulfuric and phosphoric acid solutions, respectively. It was demonstrated that that at high concentration, H_3O^+ can scavenge presolvated electrons (R6).[25] The value of C_{37}, which is defined as the solute concentration that reduces the initial yield of solvated electrons by $1/e$, is ca. 3.5 mol L^{-1}. Therefore, the scavenging of presolvated electrons in these acidic solutions is not negligible. In sulfuric acid, even at 6 mol L^{-1} the decay of the solvated electron is complete within the duration of the electron pulse but in phosphoric acid this decay is slower due to a lower concentration of free H_3O^+. The decay of $H_2O^{\bullet+}$ in pure water is due to reaction (R2) and (R7); in concentrated acid solutions additional reaction (R5) with the solute occurs. At high concentration of H_3O^+, the electron is scavenged efficiently by H_3O^+ (R6) and the geminate recombination (R7) becomes less efficient. Thus, in sulfuric acid more $H_2O^{\bullet+}$ species become

available for reacting with the solutes compared to the solutions of phosphoric acid that contain lower concentration of free H_3O^+. For these two reasons, lower probability of reaction between $H_2O^{\bullet+}$ and phosphoric acid (due to the formation of dimer in highly concentrated phosphoric acid) and lower yield of $H_2O^{\bullet+}$ (more efficient reaction (R7)), the yield of phosphate radical formed by $H_2O^{\bullet+}$ is lower than the yield of sulfate radical.

CONCLUSION

Picosecond pulse radiolysis of concentrated phosphoric acid solutions allowed us to estimate the radiolytic yield of electron detachment from phosphoric acid to be $3.7 \pm 0.1 \times 10^{-7}$ mol J^{-1}. In addition, we observed the oxidation of phosphoric acid by $H_2O^{\bullet+}$. The radiolytic yield of phosphate radical formation through water hole scavenging depends on the concentration of the phosphoric acid; in general, it is lower than the oxidation yield in sulfuric acid solutions of the same concentration. The main reason for this difference is attributed to the formation of dimer species in the concentrated phosphoric acid and lower yield of $H_2O^{\bullet+}$ due to more efficient geminate recombination in the phosphoric acid solutions. The present approach to form the phosphate radical can be used to observe the electron transfer reaction from this radical to other solutes, such as bases of DNA. Some of these reactions do not depend on pH of the solution and then it becomes possible to determine the rate constant of reactions that are involved in DNA damage.

AUTHOR INFORMATION

Corresponding Author
*E-mail: mehran.mostafavi@u-psud.fr.
Notes
The authors declare no competing financial interest.

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