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Femtosecond Spectroscopy of an Encounter Pair Radical $(H_3O^+\cdots e^-)_{hyd}$ in Concentrated Aqueous Solution

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Abstract: The spectral properties and the lifetime of an encounter pair $(H_3O^+{:}e^-)_{hyd}$ produced by femtosecond ultraviolet photolysis of concentrated hydrochloric acid aqueous solutions have been investigated at 294 K. For 11 M HCl with $R = [H_2O]/[HCl] = 5$, the transient absorption spectrum obtained following the electron detachment from chloride ion consists of three bands ($\lambda^{(1)}_{max} < 1$ eV, $\lambda^{(2)}_{max} = 1.35$ eV, $\lambda^{(3)}_{max} = 1.72$ eV) that are respectively assigned to a prehydrated electron (e^-_{prehyd}), an encounter electron–ion pair $(H_3O^+{:}e^-)_{hyd}$, and a fully relaxed electron (e^-_{hyd}). The encounter pair involving the hydronium ion and an epithermal electron $(H_3O^+{:}e^-)_{hyd}$ is characterized by a near-infrared absorption band that peaks around 920 nm. This transient species appears following a pseudo-first-order kinetics with a time constant of 250 fs. The following single exponential relaxation of this induced absorption corresponds to the deactivation of the transient encounter pair. The cleavage rate constant $[(H_3O^+{:}e^-)_{nH_2O} \rightarrow H_2O + H]$ is measured to be 1.17×10^{12} s^{-1} at ambient temperature. These data bring direct evidence that, in concentrated hydrochloric acid aqueous solution, a fast step of single electron transfer reaction is involved in the formation of a short-lived reactive configuration (encounter pair). This electron transfer occurs in a time (250 fs) that is short as compared to the electron solvation dynamics (550 fs). It is interesting to notice (i) that the encounter pair deactivation occurs through a monoexponential process and (ii) the relaxation dynamics is faster than the average lifetime of the hydrated hydronium ion but is comparable to the H-bond time scale. The mechanism of the encounter pair relaxation will be discussed taking into account the interactions between the hydronium ion and water molecules.

In chemistry and biology, charge transfers play important roles for many bimolecular reactions and the effect of solvent (nonpolar liquids and water) is fundamental especially during single electron and proton transfers.[1] In this respect, reactions of electron prior to its solvation remain to be clarified, and the nature of the primary steps involved in the reactivity of localized or hydrated electron with concentrated aqueous solutions of organic or inorganic acceptors represents a fundamental aspect of single electron transfer occurring in ultrafast radical reactions.[2-4]

Nanosecond and picosecond pulse radiolysis studies of aqueous solutions have been extensively performed to investigate (i) the fate of spatial distribution of primary radical species in tracks or spurs and (ii) the mechanism of single electron transfer in concentrated aqueous solutions.[5-10] Indirect methods including the study of initial yields of hydrated electron and the determination of the C_{37} values of a scavenger have been developed to investigate free-radical reactions occurring at the earlier times after the energy deposition in the condensed media.[11-13] In concentrated aqueous solutions, it has been suggested that excess electron can react with scavengers via the formation of an electron ion pair or an encounter pair.[14,15] While in nonpolar liquids irradiation of aromatic solutes with intense laser pulses has permitted the direct observation of short-lived electron–cation pairs,[16-20] there is, up to now, no pertinent experimental study that directly demonstrates the formation of an encounter ion pair in concentrated aqueous media at ambient temperature.

Recently, femtosecond investigations on the reactivity of excess electron in pure liquid water have shown that a non-negligible fraction of hydrated electron population (45–50%) reacts quickly with the two possible nearest neighbors (H_3O^+ and OH) produced during the pulse photolysis of water molecules.[21,22] In our experimental work, the dynamic behavior of the electron–ion pair has been considered as a reactional model in which the electron–radical pairs ($H_3O^+\cdots e^-$ or $OH\cdots e^-$) execute a one-dimensional walk before undergoing a geminate recombination with a jump rate of 0.87×10^{12} s^{-1}. However, the investigations with pure liquid water did not yield by themselves the specific role of the hydrated proton (H_3O^+) in this early free radical reaction.[22] The knowledge of free-radical reactions involving electron and proton in aqueous solutions requires direct spectral and dynamic information on the encounter pair formation between excess electron and hydronium ion.

In acid media, the reaction rate between the hydrated electron and proton (hydronium ion, H_3O^+) is smaller than the calculated bimolecular rate defined as the diffusion controlled limit process (eq 1). Furthermore, this electron scavenger does not reduce the initial yield of hydrated electron.[3] This phenomena represents an important exception to the usual relationship linking C_{37} to $k\ (e^- + H_3O^+)$,[4] which is attributed to the formation of an encounter pair $(H_3O^+{:}e^-)_{hyd}$ (eq 2).

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(1) Grimshaw, J.; Thompson, N. *J. Electroanal. Chem.* **1986**, *205*, 35.

(2) Wolfe, R. K.; Bronskill, M. J.; Hunt, J. W. *J. Chem. Phys.* **1970**, *53*, 4211.

(3) Czapski, G.; Peled, E. J. *J. Phys. Chem.* **1973**, *73*, 893.

(4) Lam, K. Y.; Hunt, J. W. *Int. J. Radiat. Phys. Chem.* **1975**, *7*, 317.

(5) Aldrich, J. E.; Lam, K. Y.; Shragge, P. C.; Hunt, J. W. *Radiat. Res.* **1975**, *63*, 42 and references therein.

(6) Chase, W. J.; Hunt, J. W. *J. Phys. Chem.* **1975**, *79*, 2835.

(7) Baxendale, J. H. *Can. J. Chem.* **1977**, *78*, 1996.

(8) Jonah, C. D.; Matheson, M. S.; Miller, J. R.; Hart, E. J. *J. Phys. Chem.* **1976**, *80*, 1267.

(9) Chernovitz, A. C.; Jonah, C. D. *J. Phys. Chem.* **1988**, *92*, 5946.

(10) Klassen, N. V. In *Radiation Chemistry*; Farhataziz, Rodgers, Eds.; VCH Publishers: Weinheim, 1988; p 29 and references therein.

(11) Razem, D.; Hamill, W. H. *J. Phys. Chem.* **1977**, *81*, 1625.

(12) Jonah, C. D.; Miller, J. R.; Matheson, M. S. *J. Phys. Chem.* **1977**, *81*, 1618.

(13) Okazaki, K.; Freeman, G. *Can. J. Chem.* **1978**, *56*, 2313.

(14) Kroh, J.; Polevoi, P. *Radiat. Phys. Chem.* **1978**, *11*, 111.

(15) Kondo, Y.; Aykawa, M.; Sumiyoshi, T.; Katayama, M.; Kroh, J. *J. Phys. Chem.* **1984**, *80*, 2544.

(16) Braun, C. L.; Scott, T. W. *Radiat. Phys. Chem.* **1988**, *32*, 315 and references therein.

(17) Miyasaka, H.; Masuhara, H.; Mataga, N. *J. Phys. Chem.* **1985**, *89*, 1631.

(18) Mataga, N. *Radiat. Phys. Chem.* **1988**, *32*, 177.

(19) Bowman, R. M.; Lu, H.; Eisenthal, K. B. *J. Chem. Phys.* **1988**, *89*, 606.

(20) Gauduel, Y.; Migus, A.; Antonetti, A. In *Chemical reactivity in liquid; fundamental aspects*; Moreau, M., Turcq, P., Eds.; Plenum: New York, 1988; pp 15-32.

(21) Lu, H.; Long, F. H.; Bowman, R. M.; Eisenthal, K. B. *J. Phys. Chem.* **1989**, *93*, 27.

(22) Gauduel, Y.; Pommeret, S.; Migus, A.; Antonetti, A. *J. Phys. Chem.* **1989**, *93*, 3880.

0002-7863/90/1512-2925$02.50/0

$$e^-_{hyd} + H_3O^+ \rightarrow H + H_2O\ (k = 2.1 \times 10^{10}\ M^{-1}\ s^{-1}) \quad (1)$$

$$e^-_{qf} + nH_2O + H_3O^+ \rightarrow (e^-\cdots H_3O^+)_{hyd}\ \text{(encounter pair)} \rightarrow e^-_{hyd} + H_3O^+ \rightarrow H_2O + H \quad (2)$$

The aim of this paper is therefore to investigate the primary steps of a fast photoinduced single electron transfer in aqueous solution containing a high concentration of hydronium ion and to determine if, in such conditions, an encounter pair $(e^-_{hyd}\cdots H_3O^+)_{hyd}$ can be directly observed at ambient temperature.

Experimental Section

Ionic aqueous solutions (HCl, LiCl) were prepared from doubly deionized water, doubly distilled in a quartz distillator with $KMnO_4$. At 294 K, the pH was 6.5 and the resistivity greater than 19 Mohms. The sample solutions were deoxygenated by tonometry with pure nitrogen gas. HCl (Merck) and anhydrous LiCl (Aldrich Chemical Co., 99.99%) were of the highest purity available and were used without further purification. Femtosecond time resolved spectra of concentrated hydrochloric acid aqueous solution have been compared to those obtained with neutral ionic solution in which the soluble lithium salt has been used in the place of H^+_{hyd}. For both concentrated HCl and LiCl aqueous solutions, we have used a molar ratio of 5 (R = mole of water/mole of XCl = 5; X = H^+ or Li^+).

The photochemical experiments performed at 294 K take place in a fixed volume suprasil cell (2 mm path length) which is stated in a plane perpendicular to the propagation of the light beams so that each successive pulse excited a new region of the sample every 100 ms. A detailed description of the femtosecond source and the optical detection equipment have been published elsewhere.[23] The pulses generated in this laser are as short as 80 fs and the wavelength is centered around 620 nm.[24] In our particular experiments, one part of the initial pulse is focused into a KDP crystal to produce up to 5–10 μJ at 310 nm constituting the pump. The ultraviolet femtosecond pulses (E = 4 eV, $I = 10^{15}$ W/m^2) are used to initiate the photodetachment of an epithermal electron from a chloride ion. For a given wavelength the signals corresponding to the probe and reference pulse energies were transferred to an electronic chain, to a HP computer, and stored on disk for further processing. The signal-to-noise ratio was enhanced by multiscan averaging. Typically over 5×10^4 pulses are taken into account to achieve a kinetic curve. The transient species following the photoionization step were then directly defined by monitoring the sample optical densities as a function of wavelength and time delay.

The transient spectra are reconstructed from experimental kinetics data performed at different wavelengths in the visible and the infrared taking into account the amplitude of the signal at each test wavelength. Due to the large spectral region under investigation (typically from 500 to 1250 nm) the chirp of the continuum induces an important shift of the zero (temporal overlap between the pump and the probe). Therefore careful experiments are simultaneously conducted at each wavelength to determine the zero time delay and the time response function of the apparatus. The total absorbance of the test pulse corresponds to an expression that takes into account all the population evolutions occurring during the excitation and probe. For each test wavelength and from the instantaneous responses obtained in pure hydrocarbon (n-heptane) we deduce the pulse shape and the actual position of the zero time delay, i.e. the position of the delay line for which the pump and the probe pulses overlap exactly. The precise procedures have been previously described in detail elsewhere.[20]

Results

1. Initial Charge Separation and Spectral Identification of the Primary Species. The induced absorption changes obtained following the femtosecond ultraviolet photoionization of concentrated hydrochloric aqueous solution (HCl 11 M, R = 5) are represented in Figure 1. The transient differential spectra showing up in the visible and the near-infrared (520–1250 nm) correspond to unstabilized species that rapidly disappear.

From transient optical absorption obtained in concentrated aqueous HCl solution, the early steps following the femtosecond excitation process of Cl^- can be described by eqs 3 to 5. It can be suggested that the femtosecond photolysis channel occurs through a highly excited state of chloride ion that can ionize to give an epithermal electron (electron photodetachment by CTTS).

Table I. Characteristic Parameters of the Component Bands in Induced Absorption Spectrum for Pure Liquid Water and Concentrated Aqueous Hydrochloric Acid Solution, [H2O]/[HCl] = 5

	λ_{max}			
	pure liquid water		$[H_2O]/[HCl] = 5$	
transient species	nm	eV	nm	eV
$[e^-_{localized}]_{IR}$	>1250	<1	>1250	<1
$[e^-_{hydrated}]_{vis}$	720	1.72	720	1.72
$[H_3O^+\cdots e^-]_{hyd}$			920	1.35

Table II. Ratio of Maximum Signal Obtained in Infrared (1250 nm) over Near-Infrared (920 nm) and Visible (720 nm) Spectral Regions Following Femtosecond Ultraviolet Photoionization of Pure Liquid Water or Concentrated Aqueous Hydrochloric Acid Solution, $[H_2O]/[HCl] = 5$

molar ratio	H_2O	$[H_2O]/[HCl] = 5$
ΔA 1250 nm/ΔA 720 nm	1.1	0.73
ΔA 1250 nm/ΔA 920 nm	1.4	0.57

$$Cl^- + h\nu\ (310\ nm) \rightarrow [Cl^-]^* \rightarrow Cl + e^- \quad (3)$$

A high energy tail of an infrared band extending above 1250 nm appears early, i.e. within the femtosecond ultraviolet excitation, and is fully developed after a delay of 500–600 fs (Figure 1A). This infrared band then totally disappears in the following 4.2 ps (Figure 1B). In agreement with our previous femtosecond experiments performed in pure liquid water and organized aqueous assemblies,[20,25,26] the early species absorbing in the near-infrared has been identified as a localized state of excess electron, i.e. an incompletely relaxed electron (precursor of the hydrated electron).[25,26]

$$e^-_{qf} + nH_2O \rightarrow e^-_{prehyd} \rightarrow e^-_{hyd} \quad (4)$$

A second important structureless spectral distribution is clearly observed between 800 and 1000 nm following femtosecond ultraviolet excitation of the concentrated hydrochloric acid aqueous solution. We assign this intense band which peaks around 920 nm (E = 1.35 eV) to an electron–cation pair $(H_3O^+\cdots e^-)_{hyd}$ composed of an excess electron and a hydrated hydronium ion $(H_3O^+)_{nH_2O}$ (eq 5). No significant spectral shift is observed during the risetime and the relaxation of this near-infrared absorption band (Figure 1A,B).

$$e^-_{qf} + (H_3O^+)_{nH_2O} \rightarrow (e^-{:}H_3O^+)_{nH_2O}\ \text{(encounter pair)} \quad (5)$$

Looking toward the shorter wavelength (λ < 800 nm), a third spectral component can also be observed after the femtosecond photoionization of the concentrated HCl aqueous solution. This unstructured band peaks around 700 nm and coincides with the known hydrated electron band. Consequently, we assign this hump to an electron stabilized in normal aqueous traps (E = 1.72 eV), i.e. to a fully hydrated electron similar to what is occurring in dilute aqueous solutions or pure liquid water $(e^-)_{hyd}$. Furthermore, we do not observe significant blue shift of this band (Figure 1, Table I), as compared to the transient spectral absorption of the hydrated electron obtained in dilute aqueous solution (λ_{max} = 720 nm).

It is interesting to notice that 4 ps after the femtosecond photoexcitation process, a weak absorption containing two humps is still observed in the spectral range 500–950 nm (Figure 1B). These bands are due to the presence of residual hydrated electron and non-fully relaxed encounter pair in the aqueous medium.

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[23] Gauduel, Y.; Migus, A.; Martin, J. L.; Lecarpentier, Y.; Antonetti, A. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 218.

[24] Migus, A.; Antonetti, A.; Etchepare, J.; Hulin, D.; Orszag, A. *J. Opt. Soc. Am.* **1985**, *B2*, 584.

[25] Gauduel, Y.; Berrod, S.; Migus, A.; Yamada, N.; Antonetti, A. *Biochemistry* **1988**, *27*, 2509.

[26] Gauduel, Y.; Martin, J. L.; Migus, A.; Antonetti, A. In *Ultrafast Phenomena V*; Fleming, Siegman, Eds.; Springer Verlag: New York, 1986; p 308. Migus, A.; Gauduel, Y.; Martin, J. L.; Antonetti, A. *Phys. Rev. Lett.* **1987**, *58*, 1559.

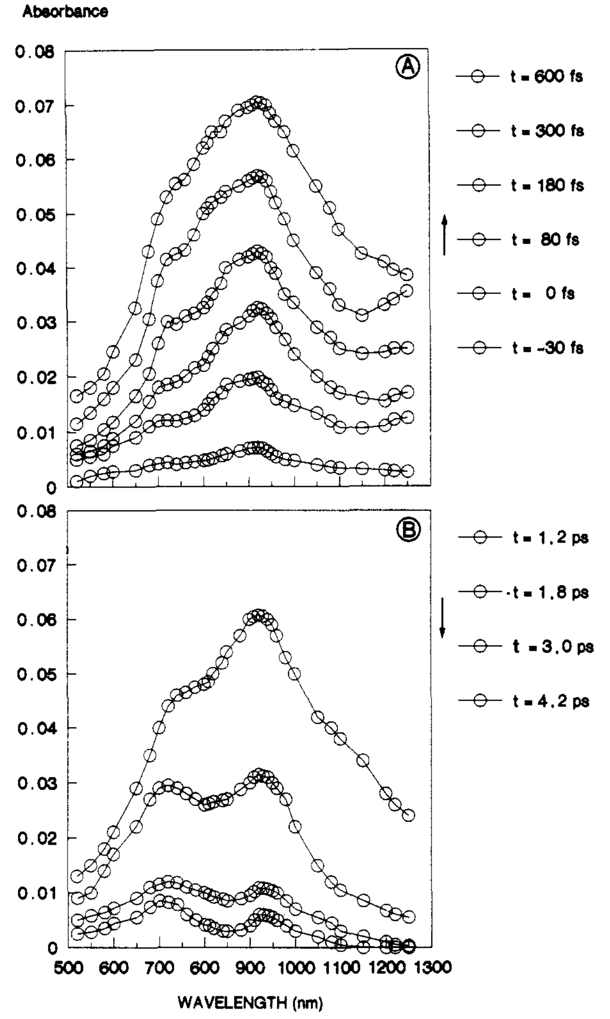

Figure 1. Transient absorption spectra obtained at different times (from −30 fs to 4.2 ps) after femtosecond photoionization of concentrated aqueous solution of HCl (11 M, $R = [H_2O]/[HCl] = 5$) at 310 nm ($E = 4$ eV). The points are calculated from the experimental kinetics and the amplitude of the signal obtained at different wavelengths.

A comparison of the characteristics of transient spectra obtained in pure liquid water and concentrated HCl aqueous solutions ($R = 5$) is summarized in Table II. These data indicate that the ratio of the more infrared band to the other ones decreases when the proton concentration increases. Similar results are obtained in concentrated ionic aqueous solutions containing Na^+ or Li^+.[27]

2. Dynamics of Electron Trapping and Solvation in Concentrated HCl Aqueous Media. Our experimental results allow us to directly determine the dynamics of the early events leading to the formation of the primary species, i.e. the localized state of electron (e^-_{prehyd}), the hydrated state (e^-_{hyd}), and the encounter pair $(H_3O^+\cdots e^-)_{hyd}$.

The analysis of the time-resolved spectroscopic data in the near-infrared and the visible spectral region has been conducted with a kinetic model in which the behavior of the total induced absorbance has been analyzed, for each test wavelength, considering the convolution of the pump–probe pulses temporal profile and the expected signal rise dynamics including the different transient species (i = localized electron, fully hydrated electron, encounter pair):

$$\Delta A^\lambda(\tau) = \sum C_i \epsilon_i l = \sum A_i^\lambda(\tau) \qquad (6)$$

The evolution of the different populations during the pumping and probing follows the expression

$$\Delta A_i^\lambda(\tau) = \epsilon_i^\lambda l \int_{-\infty}^{+\infty} C_i(\tau - \tau')C(\tau')\,d\tau' \qquad (7)$$

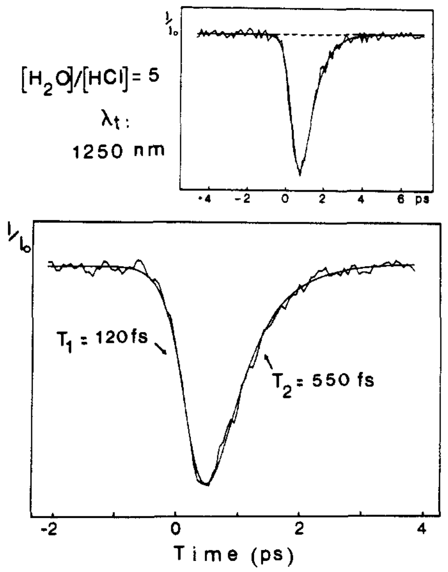

Figure 2. Time-resolved induced absorption at 1250 nm following femtosecond UV excitation of concentrated hydrochloride acid aqueous solution (11 M) at ambient temperature. The smooth lines represent the best computed fits of the experimental data. At 1250 nm, the computed fit assumes an appearance time of 120 fs for the precursor of hydrated electron and its complete relaxation following a pseudo-first-order process ($\exp(-t/T)$) with $T = 550$ fs.

In these expressions, l is the interaction length, ϵ^λ the molar extinction coefficient, $C^\lambda(\tau')$ the normalized correlation between the probe and the pump pulse, and C_i the concentration of species i.

The interaction of UV laser pulses, which have a low ionization potential, with chloride ion leads to an ultrafast charge separation ($Cl\cdots e^-$) in the aqueous phase or in the vicinity of the hydrated proton (H_3O^+). Similar primary ionization steps obtained with polycyclic chromophore (phenothiazine) entrapped in organized assemblies have shown that the dynamics of excess electron ejection ($A \rightarrow A^+ + e^-_{qf}$) is limited by the instrumental response.[25]

The kinetics of the induced absorption obtained in the infrared is shown in Figure 2. The model used to fit these data assumes that the risetime of the transient absorbance at 1250 nm occurs with a time constant T_1 and that the species (e^-_{prehyd}) relaxes toward the solvated state, following a pseudo-first-order kinetics with a time constant T_2 (eq 8).

$$(C_e^-)_{IR}(t) = C^0[T_2/(T_2 - T_1)][T_2 \exp(-t/T_2) - T_1 \exp(-t/T_1)] \qquad (8)$$

The best computed fit of the experimental curve taking into account the convolution of the apparatus time with the infrared electron population evolution (eq 8) gives $T_1 = 120$ fs and $T_2 = 550$ fs. The good agreement assuming a single exponential relaxation law suggests that the mechanism corresponds to the transition of a single state (presolvated state of electron or localized electron) toward a fully hydrated state (eq 4). We find the IR relaxation rate constant equals $1.81 \times 10^{12}\ s^{-1}$ at 294 K. This value is lower than those obtained in pure liquid water ($4.1 \times 10^{12}\ s^{-1}$). In the specific case of concentrated HCl aqueous solutions, the recovery of the signal at 1250 nm is complete (Figure 2). This result means that there is no significant contribution of other population in this infrared spectral region.

3. Femtosecond Formation of an Encounter Pair $(H_3O^+{:}e^-)_{hyd}$ in Aqueous Media. The good resolution of the early steps following femtosecond photoionization of concentrated hydrochloric acid aqueous solution allows us to consider a specific photochemical channel in which an excess electron will be ejected inside the hydration shell of a hydronium ion $(H_3O^+)_{nH_2O}$.

Figure 3B,C,D shows the risetime of the induced absorption at three different wavelengths in the visible and its decay as a function of the pump–probe time delay. These curves have been analyzed considering the convolution of the pump–probe pulses,

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[27] Gauduel, Y.; Pommeret, S. In preparation.

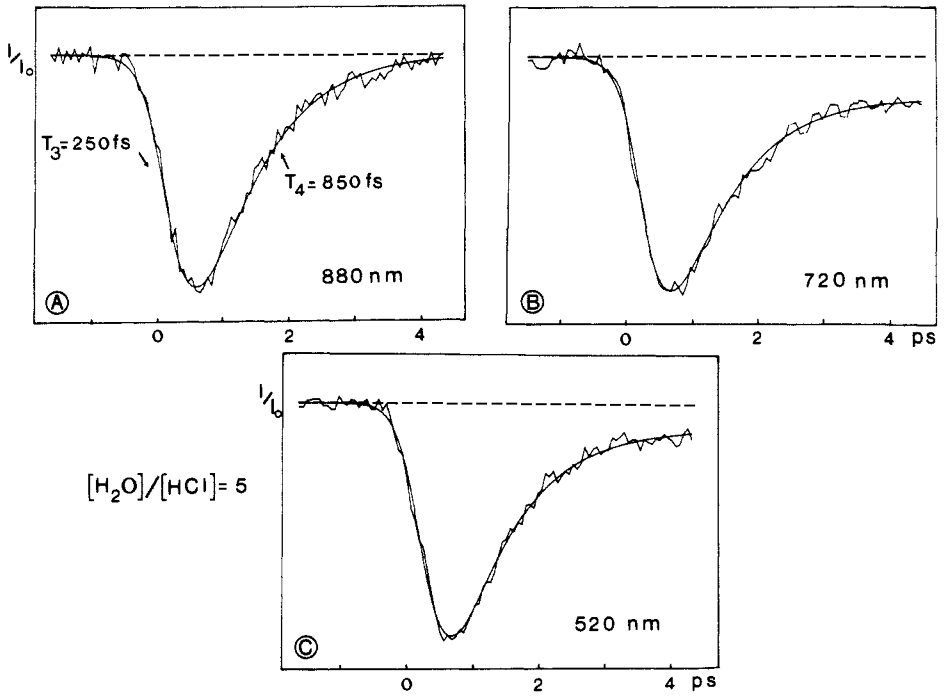

Figure 3. (A) Risetime of the induced absorption at 880 nm showing the dynamics of formation of the encounter pair between excess electron and hydroxonium ion (H_3O^+) in concentrated hydrochloride acid aqueous solution ($[H_2O]/[HCl] = 5$). This transient species $(H_3O^+{:}e^-)_{hyd}$ appears with a time constant T_3 of 250 fs and disappears following a monoexponential law in 850 fs. (B, C) At 720 and 520 nm the risetime of the induced absorption results from the combination of two processes. The first one, electron hydration, occurs through the formation a localized prehydrated state with an appearance time T_1 = 120 fs and a lifetime T_2 = 550 fs. The second one corresponds to the formation of an encounter pair $(H_3O^+\cdots e^-)_{hyd}$ in 250 fs with a mean lifetime of 850 fs as shown at 880 nm.

the expected signal rise dynamics of electron solvation (e^-_{hyd}), and the contribution of a transient encounter pair ($H_3O^+{:}e^-$) including the hydronium ion H_3O^+ or its hydrated state $(H_3O^+)_{nH_2O}$.

$$\Delta A^\lambda(\tau) = \Delta A^\lambda_{e^-hyd}(\tau) + \Delta A^\lambda_{(H_3O^+\cdots e^-)_{hyd}}(\tau) \qquad (9)$$

The evolution of the two populations during the pumping and probing follows the expressions

$$\Delta A_1^\lambda(\tau) = \epsilon^\lambda_{e^-_{hyd}} l \int_{-\infty}^{+\infty} C_1(\tau - \tau')C(\tau')\, d\tau' \qquad (10)$$

$$\Delta A_2^\lambda(\tau) = \epsilon^\lambda_{e^-:H_3O^+} l \int_{-\infty}^{+\infty} C_2(\tau - \tau')c(\tau')\, d\tau' \qquad (11)$$

The concentration (C_1) of hydrated electron created at a time t has been estimated following a three-level scheme

$$C_1(t) = C^0{}_1[1 - 1/(T_2 - T_1)][T_2 \exp(-t/T_2) - T_1 \exp(-t/T_1)] \quad (12)$$

In this equation T_1 represents the dynamics of electron localization in the aqueous phase and T_2 the dynamics of relaxation of localized electron. We have used the time constant T_1 = 120 fs and T_2 = 550 fs which have been determined in the infrared.

The second contribution ($\Delta A_2^\lambda(\tau)$) represents the formation of the encounter pair $(H_3O^+\cdots e^-)_{hyd}$. This species appears with a time constant T_3 and the concentration (C_2) created at a time (t) has been determined by the expression

$$C_2(t) = C^0{}_2[T_4/(T_4 - T_3)][\exp(-t/T_4) - \exp(-t/T_3)] \qquad (13)$$

In expression 13, T_3 is the appearance time constant of the encounter pair and T_4 the lifetime of this transient species.

The kinetics of appearance of the induced absorption is perfectly fitted to the convolution of the pulse profile and the linear combination of a two-signal rise $\alpha\Delta A_1^\lambda(\tau) + \beta\Delta A_2^\lambda(\tau)$ assigned to e^-_{hyd} and $(H_3O^+)_{hyd}$, respectively (Figure 3 and Table III). The contribution of the hydrated electron population explains the incomplete recovery of the signal in the visible spectral region (520, 720, 880 nm). The encounter pair $(H_3O^+\cdots e^-)_{hyd}$ absorbs in the red spectral region and the near-infrared with a maximum around 920 nm (Figure 1A). At 880 nm, i.e. near the maximum of the band assigned to the encounter pair, the contribution of this species represents 95% of the signal.

Table III. Variation of the Coefficients α and β Corresponding to the Percentage of Contribution of the Different Populations for Prehydrated or Hydrated Electron (α) and Encounter Pair (β) Generated in Concentrated Hydrochloric Acid Aqueous Solution after Femtosecond Ultraviolet Pulse

	wavelength, nm				
	520	660	720	880	1250
α	0.11	0.13	0.18	0.05	1
β	0.89	0.87	0.82	0.95	0

For the three test wavelengths (880, 720, 520 nm), T_3 is found to be 250 fs (Figure 3). The femtosecond experiments performed in the visible spectral region indicate also that the radical pair relaxes following a single monoexponential law ($\exp(-t/T_4)$). The convolution of the pulse shape with the dynamics of the different populations implies for T_4 a value of 850 fs (Figure 3B,C). This time constant remains independent of the test wavelength. This suggests that (i) there is no observable spectral modification during the relaxation process and (ii) the relaxation of an encounter pair or a geminate electron-ion pair should correspond to a single transition state (eq 14)

$$(H_3O^+)_{hyd} + e^-_{qf}\ (k_3) \rightarrow [(H_3O^+{:}e^-)_{hyd} \leftrightarrow (H_3O)^*_{hyd}]\ (k_4) \rightarrow H + H_2O \quad (14)$$

$$\text{with } k_3 = 1/T_3 \text{ and } k_4 = 1/T_4$$

Since the mean lifetime of this encounter pair $(H_3O^+{:}e^-)_{nH_2O}$ is shorter than 1 ps, it can be concluded that the influence of a diffusion process remains negligible during the relaxation step.

It is interesting to notice that the lifetime of this encounter pair is true to that of hydronium ion and not that of chloride ion. In equivalent concentrated aqueous solutions in which the lithium ion is put in place of H_3O^+, the lifetime of the new encounter pair $(Li^+{:}e^-)_{nH_2O}$ is significantly increased (Figure 4). The reactivity of chloride atom (Cl) or Li^+ with electron remains negligible in the first 20 ps following photoionization of chloride ion.

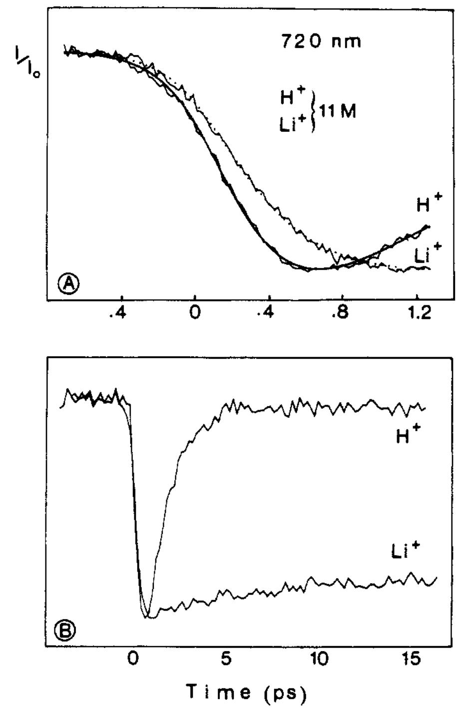

Figure 4. Influence of the counterion (H^+ or Li^+) on the risetime and the behavior of excess electron following femtosecond UV photoionization of concentrated aqueous chloride solutions (HCl = LiCl = 11 M, λ_t = 720 nm). (A) In concentrated aqueous solution of H_3O^+, the smooth line represents the best computed fit of the experimental trace assuming an electron solvation time of 550 fs and an average encounter pair lifetime of 850 fs. In LiCl 11 M, electron solvation occurs with a time constant of 550 fs. (B) In acid aqueous solution, the induced absorption decreases according to a monoexponential law. A similar relaxation is not observed in concentrated LiCl aqueous solution.

A comparison of the relaxation law of this electron–ion pair with previous results obtained on electron recombination in pure liquid water at ambient temperature is shown in Figure 5. The difference of the relaxation route can be attributable to a significant modification of the initial charge distribution (electron–hydronium ion) going from neat water to hydrochloric aqueous solutions. In pure liquid water the probability of an encounter pair formation remains low because the concentration of electron scavenger (H_3O^+) is in the micromole range. In these conditions, our previous femtosecond investigations have demonstrated that near 50% of the excess electrons escape far from the geminate primary radical H_3O^+ or OH. Consequently, the early recombination corresponds to the reactivity of the electrons that are hydrated in the vicinity of their geminate counterion (H_3O^+/OH) and that recombine by executing a one-dimensional (1D) walk.[22]

In concentrated aqueous hydrochloric acid solution, the high concentration of hydronium ion would favor the localization of a significant fraction of excess electron in the solvation shell of the cation $[(H_3O^+)_{nH_2O})]$. In these conditions, the probability P' ($P' = 1 - \exp(-4\pi r_{eff}^3[S]/3 \times 10^3)$) that an excess electron is inside the encounter volume is not negligible when the concentration of the hydronium is 11 M. Let us check this point: the effective reaction radius has been calculated from the expression related to the C_{37} values: $r_{eff} = 7.35C_{37}^{-1/3}$.[4] In water, the C_{37} value of H_3O^+ equals 10 M and the estimate of r_{eff} is 3.41 Å. Reporting this value in expression 9, we obtain $P' = 0.84$ for the probability of an encounter pair formation in aqueous hydrochloric acid solution ($[H_2O]/[HCl] = 5$). Consequently, as shown in Figure 6, the channel corresponding to electron localization and solvation outside the hydration shell of H_3O^+ represents about 16% of the single electron transfer.

Discussion

The reactivity of an epithermal electron in concentrated hydrochloric acid aqueous solution has been investigated by time-resolved spectroscopy in the femtosecond regime.

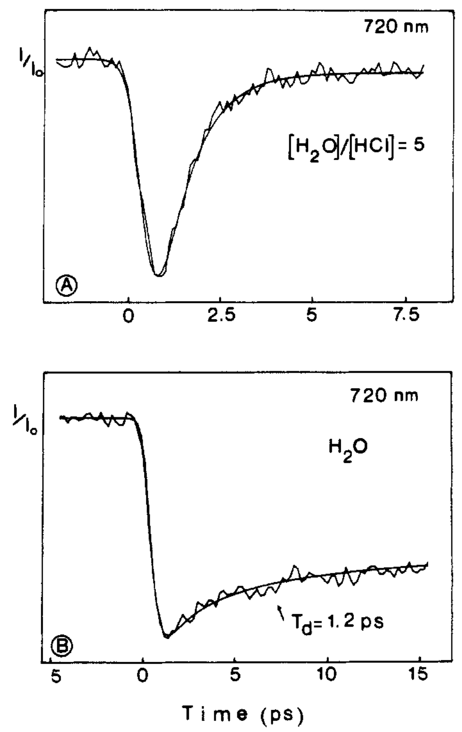

Figure 5. Comparison in the time dependence of the induced absorbance at 720 nm following the femtosecond photoionization of concentrated hydrochloride acid aqueous solution (A) and pure liquid water (B). In aqueous acid solution ($[H_2O]/[HCl] = 5$), the absorption decay corresponding to the deactivation of the encounter pair $(H_3O^+{:}e^-)_{hyd}$ is well fitted to a monoexponential law ($\exp(-t/T)$ with T = 850 fs. The incomplete recovery of the signal is due to the contribution of the hydrated state of electron. In pure water, the computed best fit of the early decay gives a random walk law [$A = A^0 \operatorname{erf}(T_d/t)^{1/2}$] with T_d = 1.2 ps.

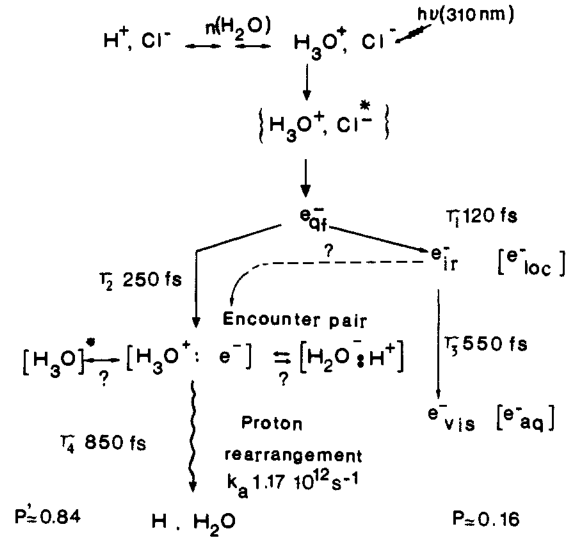

Figure 6. Sequence of primary photochemical events occurring in concentrated hydrochloride acid aqueous solution $[H_2O]/[HCl] = 5$ following femtosecond UV excitation. This figure shows the two single electron transfer channels leading to the formation of hydrated electron ($P \sim 0.16$) and the encounter radical pair $(H_3O^+{:}e^-)_{hyd}$ ($P' \sim 0.84$).

These femtosecond photochemical investigations demonstrate that the ultraviolet photoionization of concentrated aqueous acid solution induces two single electron transfer channels (Figure 6). The first one corresponds to a coupling between excess subexcitation electron and water molecules. This single electron transfer leads to electron hydration and occurs through an intermediate state identified as the precursor of the fully hydrated electron. In concentrated acid media where the number of water molecules involved in the hydration of H^+ and Cl^- equals 5, the trapping time (120 fs) remains similar to values obtained in pure liquid water at ambient temperature (110 fs).[26] Similar results have been obtained with other ionic aqueous solutions at different concentrations ($FeCN_6K_4$ 0.48 M, LiCl 11 M). These dynamical data suggest that neither the mode of electron photoejection (solute or solvent molecules) nor the nature of the cation influence the rate of energy deposition and electron trapping.

Several authors have previously discussed the diffferences in the absorption and Raman spectra of pure water and electrolyte solutions[28-30] and shown that in acid solutions the polarizability of hydrogen bonds is changed compared to that in pure liquid water (H-O-H).[31] In the specific case of concentrated hydrochloric acid aqueous solutions, it seems that the dynamics of the early steps of electron-water interactions (electron thermalization and localization) is dependent neither on large intermolecular rearrangements of solvent molecules nor on structural changes of the three-dimensional hydrogen-bonded network of water molecules in the vicinity of the hydronium ion.

It is interesting to notice that in concentrated aqueous solutions containing XCl ($X = H^+, Li^+, Na^+$) the amplitude of the infrared signal assigned to a non-fully hydrated electron decreases. It seems reasonable to assume that in such ionic aqueous solutions, the density and configurational fluctuations provide a potential well into which the excess epithermal electron may be directly localized. In this hypothesis, the favorable spatial distribution of deep traps created by the presence of negative ion would represent a specific order of the liquid for direct electron hydration.[32,33]

Recent experimental and theoretical studies on femtosecond molecular motions in liquid water have proposed that the librational motion of water, representing the configurational disorder of the "frozen" liquid at the 10^{-14} s time scale, will be involved in the initial localization process.[34-36] Actually, considering that we have no available information on the instantaneous concentration of trapped electron, the ionic effect on the configurational disorder remains to be clarified, in particular the role of local ionic strength and electronic field on the fluctuations due to translational and reorientational motions of the water molecules and on the oscillator strength of the non-fully solvated electron.

Our femtosecond results obtained in concentrated hydrochloric acid aqueous solution demonstrate that the final relaxation step of the localized electron $(e^-)_{IR}$ occurs with a rate constant that is smaller than in pure water or dilute ionic aqueous solutions: $1.8 \times 10^{12}\ s^{-1}$ against $4.16 \times 10^{12}\ s^{-1}$. These time-resolved data confirm previous results obtained in small water clusters containing a high concentration of Na^+.[37] In these media, the electron solvation dynamics remains independent on the relaxation time of the ionic atmosphere and is much faster than the formation time of Na^+ atmosphere around the hydrated electron (T_r), as estimated by the equation of Coyle et al.[38] In acid media the torsional vibration of the water molecules changes the potential well of the hydrated proton and the polarization of the hydrogen bond. Consequently, it can be suggested that in such media the electron solvation does not involve large molecular movements and remains largely independent of physical properties such as the dielectric constant, the viscosity, and the kinematic viscosity. Our results tend to indicate that in concentrated ionic aqueous media (H_3O^+ or Li^+), the electron hydration dynamics, being faster than the dielectric or longitudinal relaxation time, remain independent of dominant molecular response of the solvent.

At 294 K we have not observed a significant protonic strength effect on the hydrated electron spectrum in the range 0-11 M. This fact contrasts with the significant ionic strength effect observed with other cations (Na^+, Li^+) in concentrated aqueous solutions.[14,15,27,39-41] Consequently, the high concentration of hydronium ion in aqueous media seems not to cause the energetic complications in the electron hydration process.

The second single electron transfer channel we have observed in concentrated hydrochloric acid aqueous solution corresponds to an ultrafast coupling between an epithermal electron and the hydration shell of a hydronium ion $(H_3O^+)_{nH_2O}$. This coupling leads to the formation of an encounter pair whose direct observation is the main result of this work.

In concentrated aqueous hydrochloric acid solution with a mole ratio of 5 ($R = [H_2O]/[HCl]$), the formation of an encounter pair $(H_3O^+\cdots e^-)_{hyd}$ has been observed to follow a rate constant of $4 \times 10^{12}\ s^{-1}$. This early step, which is faster than the complete hydration of the excess electron (Figure 6), probably corresponds to a localization of the electron in shallow traps linked to the presence of hydrated hydronium ion $(H_3O^+)_{nH_2O}$. In agreement with previous pulse radiolysis investigations which suggested that, in concentrated ionic aqueous solutions, the ion pair $(Na^+\cdots e^-)_{hyd}$ should be produced at an earlier stage than the hydrated electron,[15,40] our femtosecond data clearly establish that the single electron transfer ($H_3O^+ + e^- \rightarrow H_3O^+{:}e^-$) occurs prior to the electron hydration phenomenon.

Indeed, the femtosecond photochemical investigations of concentrated hydrochloric acid aqueous solutions demonstrate that a significant fraction of electrons are directly localized in the reaction radius of the scavenger, i.e. in the hydration shell of the hydronium ion $(H_3O^+)_{nH_2O}$ or through a long-range electron tunnelling as suggested by Miller.[42] Considering the probability ($P' = 1 - P$) for an electron to be localized or hydrated in the radius of a scavenger, we get a value of 3.41 Å for r_{eff}. This estimate can be compared to structural information obtained by X-ray and neutron diffraction on hydrated hydronium ion or by ab initio calculation and Monte Carlo simulations.[43,44] Structural investigations on interaction between water molecules and hydronium ion in concentrated hydrochloric acid aqueous solutions have shown that the hydronium ion is hydrogen bound to four water molecules. The $H_3O^+\cdots OH_2$ distance is 2.52 Å against 2.76 Å in pure liquid water.[45-48] Indeed, the estimate of the effective radius agrees with the dimensions of the nearest-neighbor configurations around the hydronium ion and supports an encounter pair formation within the first solvation shell of H_3O^+.

In the discussion on the evolution of the coupling between the electron-hydronium ion pair and water molecules during the relaxation process we should wonder whether the relaxation of this encounter pair corresponds to intracomplex structural changes (i.e. geometrical perturbations of the hydration cage) considering that the ultrafast encounter pair relaxation occurs at a very short time before diffusion of proton becomes appreciable. In agreement with experimental data, ab initio calculations on the hydration of the hydronium ion have demonstrated particular structural characteristics of water molecules surrounding this ion.[48-50] In

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(28) Pernoll, I.; Maier, U. *J. Chem. Soc. Faraday Trans. 2* **1975**, *71*, 201.

(29) Hayd, A.; Weidemann, E. G.; Zundel, G. *J. Chem. Phys.* **1979**, *70*, 86.

(30) Kanno, H.; Hiraishi, J. *Chem. Phys. Lett.* **1984**, *107*, 438.

(31) Janoschek, R.; Weidemann, E. G.; Pfeifer, H.; Zundel, G. *J. Am. Chem. Soc.* **1972**, *94*, 2387.

(32) Kenney-Wallace, G. A.; Jonah, C. D. *J. Phys. Chem.* **1982**, *86*, 2572.

(33) Kenney-Wallace, G. A.; Kalpouzos, C.; Lotshaw, W. *Radiat. Phys. Chem.* **1988**, *32*, 573.

(34) Schnitker, J.; Rossky, P. J. *J. Chem. Phys.* **1987**, *86*, 3462.

(35) Mozumder, A. *Radiat. Phys. Chem.* **1989**, *34*, 1.

(36) Motakabbir, K. A.; Rossky, P. J. *Chem. Phys.* **1989**, *129*, 253.

(37) Gauduel, Y.; Pommeret, S.; Yamada, N.; Migus, A.; Antonetti, A. *J. Am. Chem. Soc.* **1989**, *111*, 4974.

(38) Coyle, P. J.; Dainton, F. S.; Logan, S. R. *Proc. Chem. Soc., London* **1964**.

(39) Hart, E. J.; Anbar, M. In *The hydrated electron*; Wiley Intersciences: New York, 1970.

(40) Woods, R. J.; Lesigne, B.; Gilles, L.; Ferradini, C.; Pucheault, J. *J. Phys. Chem.* **1975**, *79*, 2700.

(41) Kreitus, I. *J. Phys. Chem.* **1985**, *89*, 1987.

(42) Miller, J. R. *J. Chem. Phys.* **1972**, *56*, 5173; *J. Phys. Chem.* **1972**, *76*, 2641; *Chem. Phys. Lett.* **1973**, *22*, 180.

(43) O'Ferral, R. A. M.; Koeppl, G. W.; Kresge, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 1.

(44) Giguere, P. A.; Guillot, J. C. *J. Phys. Chem.* **1982**, *86*, 3231.

(45) Bell, R. A.; Christoph, G. G.; Fronczek, F. R.; Marsh, R. E. *Science* **1975**, *190*, 151.

(46) Triolo, R.; Narten, A. H. *J. Chem. Phys.* **1975**, *63*, 3624.

(47) Lee, H. G.; Matsumoto, Y.; Yamaguchi, T.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 443.

(48) Fornili, S. L.; Migliore, M.; Palazzo, M. A. *Chem. Phys. Lett.* **1986**, *125*, 419.

(49) Newton, M. D.; Ehrenson, S. *J. Am. Chem. Soc.* **1971**, *93*, 4971.

(50) Newton, M. D. *J. Chem. Phys.* **1977**, *67*, 5535.

particular the reorientational relaxation of water molecules close to the hydronium seems to be faster than in bulk water. This means that the monoexponential stabilization of this encounter pair is in agreement with a deactivation process inside a potential well involving molecules bounded to hydronium ion. In the specific case of aqueous solutions, the solvent reorganization would include the hydrogen bond restructuration in the vicinity of hydrated proton without the intervention of a significant diffusion process. We can wonder whether in concentrated aqueous acid solutions the radical ion pair deactivation occurs through two deprotonation processes of the hydrated hydronium ion. These processes would include either an early deprotonation of H_3O^+ with a subsequent neutralization of H^+ by the electron or an electron-induced OH bond cleavage leading to the generation of the hydroxyl radical (eq 15)

$$e^- + (H_3O^+)_{hyd} \rightarrow [e^-{::}H_3O^+]^*_{hyd} \rightarrow H_2O + H^\circ \rightarrow OH + H_2 \qquad (15)$$

It is interesting to notice that the cleavage rate constant of the encounter pair occurs at a similar time scale as the H-bond mean lifetime (0.58 ps at 293 K)[51] or average lifetime of the hydronium ion in liquid water.[52-54] This means that the relaxation of the encounter pair can be dependent either on the H bond dynamics between H_3O^+ and water molecules or on proton migration from hydronium to neighboring water molecules. We suggest that the limiting factor of the deactivation dynamics of the encounter pair corresponds to the activation energy of the radical–ion bond cleavage reaction including either a proton migration from hydronium ion to neighbor water molecules or a local polarization effect on H bonds. In this way, the initial reactivity of excess electron with hydrated hydronium ion $(H_3O^+ + e^-)_{hyd}$ would depend on the local structure of this cation in the vicinity of water molecules. Recent computer simulations of hydrated hydronium ion performed at 300 K have shown that the relaxation of water molecules around a new hydronium ion is a process that is faster than the lifetime of this ion.[48] In this hypothesis, the relaxation of the encounter pair can be compatible with ultrafast local reorganization of water molecules including a few vibrational periods of OH bonds or librational and translational movements of the hydronium ion.

In conclusion, transient spectra observed in the visible and near-infrared have permitted us to identify the formation of hydrated electron and encounter pair populations. In comparison with the spectrum of the stabilized hydrated electron (E_{max} = 1.7 eV), the maximum of the band assigned to the radical pair is red shifted (E_{max} = 1.35 eV). We have shown that a photochemical single electron transfer performed in concentrated acid aqueous solution induces the formation of an encounter pair involving an epithermal electron and a hydronium ion. This encounter pair formation occurs earlier than the electron hydration step. The deactivation dynamics of this radical pair (850 fs) is comparable to the estimate of the mean lifetime of the hydronium ion or H-bond. The present femtosecond spectroscopic data strongly suggest that the monoexponential relaxation of this encounter pair toward an equilibrium configuration can be triggered by a rearrangement of the hydrogen bonding to hydronium ion or an electron–proton transfer involving an hydronium ion and neighboring water molecules. Further experimental works are in progress to investigate the role of water molecules surrounding encounter pair during the deactivation step.

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(51) Conde, O.; Teixera, J. *J. Phys.* **1983**, *44*, 525.
(52) Glick, R. E.; Tewari, K. C. *J. Chem. Phys.* **1966**, *44*, 546.
(53) Rabideau, S. W.; Hetch, H. G. *J. Chem. Phys.* **1967**, *47*, 544.
(54) Halle, B.; Karlstrom, G. *J. Chem. Faraday Trans.* **1983**, *70*, 1047.

Tautomerization Energetics of Benzoannelated Toluenes

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Abstract: The energy of tautomerization of some isotoluene structures has been measured by gas-phase ion/molecule reactions and by solution calorimetry. Benzoannelation appreciably destabilizes the aromatic tautomer, relative to the isotoluene form. An inverse saturation effect on the acidities of toluene, 1-methylnaphthalene, and 9-methylanthracene is observed. The *p*-isotoluene 3-methylene-1,4-cyclohexadiene appears to have the weakest C–H bond dissociation energy known, 64 ± 3 kcal/mol. Molecular orbital calculations bear out these results.

The extra stability of aromatic compounds is such a well-documented concept in organic chemistry that there is a tendency to assume that species that can become aromatic will do so. In this light, the kinetic stability of prismane[2] and Dewar benzene, bicyclo[2.2.0]hexa-2,5-diene,[3] seems surprising at first, until the rationale of orbital symmetry forbiddeness is considered. It would be useful, however, to have some method of turning aromaticity on and off in a given structure, so that the energy difference could be determined. One possibility for this involves tautomerization, a type of isomerism involving minimal perturbation of the structure. Tautomers have the same heavy-atom connectivity, and only the attachment of the hydrogen atoms is varied. This in general allows interconversion of tautomers by Brønsted acid/base catalysis.

Such tautomers involving aromatic structures were originally not considered to be isolable, save for the case of phenol derivatives.[4] The first semiquantitative report of tautomerism as a measure of aromaticity in hydrocarbons was in 1949 by Clar and Wright,[5] for the reversible interconversion of 6-methylpentacene

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(2) Peacock, N. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1972**, *94*, 5906.
(3) Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 646.
(4) Horning, E. C. *Chem. Rev.* **1943**, *33*, 89.
(5) Clar, E.; Wright, J. W. *Nature (London)* **1949**, *163*, 921.

0002-7863/90/1512-2931$02.50/0