Supporting Information for

Broadband spectral probing reveals ultrafast photochemical branching after ultraviolet excitation of the aqueous phenolate anion

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Effect of electron quencher to the geminate dynamics of the solvated electron and radical

In electron photodetachment studies, an electron quencher is used quite frequently both for assignment of the electron's transient absorption, and to separate the dynamics of solvated electron from the rest of the species involved. The effect of the quencher to the electron population dynamics itself is well known, but it is not as clear how the geminate radical population responds to the externally added quencher. In this section, we give a general expression of the dynamics for both geminate partners when the electron quencher is present in the solution, and an analytical result is found when a bi-exponential function is used to approximate the geminate recombination dynamics.

In such a system without electron quencher, the electron and the radical are created in pairs. We use e^{-} , R_P , and (R_P-e^{-}) to represent three potential species. We do not specifically mean

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to imply that (R_P-e^-) represents a contact pair, just that their dynamics are correlated. The three share identical population dynamics during a time window during which neighboring solute molecules are too far away to reach by diffusion, because the only way their populations decay is via geminate recombination with each other to form a product, P, which here is reforming the original solute species present before photoexcitation.

$$(R_P - e^-) \to P \tag{1}$$

If the initially prepared (R_p -e⁻) population is 1 and $\Omega(t)$ is used to represent the survival probability of the generated electron, the population variation for each species can be written as

$$[R_{p}](t) = [e^{-}](t) = [(R_{p} - e^{-})](t) = \Omega(t)$$
(2)

When electron quencher Q is added to the system, it reacts with the radical/electron geminate pair (R_p-e^-) which produces unpaired radical R_{uP}

$$(R_P - e^-) + Q \to R_{uP} \tag{3}$$

In the geminate recombination time window, the R_{uP} population does not decay after it is produced, but the R_P population decreases according the relationship of (2). It should be pointed out that even though their dynamics are different due to their different surrounding, R_{uP} and R_P are spectroscopically indistinguishable, and the transient absorption measurement records the total radical population, [R](t).

$$[R](t) = [R_p](t) + [R_{uP}](t)$$
(4)

Certain types of species Q, such as the nitrate anion, can scavenge electrons in two different ways. The first is long-range occurs "instantaneously" fast and is called static quenching. The result is that at time zero, part of the potential (R_P -e⁻) population is converted to

 R_{uP} . η is used to describe the fraction of geminate pairs (R_{P} -e⁻) that have been statically quenched, and accordingly R_{uP} has population η at time zero. η is a function of the quencher concentration in the sense that more electrons are statically scavenged when [Q] is higher.¹ The other electron scavenging occurs diffusively by a slower bimolecular reaction. Because of the excess of quencher concentration under typical quenching experiment, the diffusive quenching becomes a quasi-unimolecular reaction, and the electron population acquires an extra exponential decay.

$$[R_{p}](t) = [e^{-}](t) = [(R_{p} - e^{-})](t) = (1 - \eta)\Omega(t)e^{-k_{q}[Q]t}$$
(5)

Note that η is also included to account for the amount of static quenching occurring at time zero.

According to (3), R_{uP} population can be obtained by integrating the following differential equation.

$$\frac{d[R_{uP}](t)}{dt} = k_q[Q][(R_P - e^{-})](t)$$
(6)

The temporal variation of the geminate recombination pair is already known from (5), and $[R_{uP}](t)$ has a value of η at t=0. Then the population dynamics of the unpaired radical can be written as

$$[R_{uP}](t) = \eta + \int_0^t k_q [Q](1-\eta)\Omega(\tau) e^{-k_q [Q]\tau} d\tau$$
(7)

The total radical population according to (4), (5) and (7) is then

$$[R](t) = (1 - \eta)\Omega(t)e^{-k_q[Q]t} + \eta + \int_0^t k_q[Q](1 - \eta)\Omega(\tau)e^{-k_q[Q]\tau}d\tau$$
(8)

If $\Omega(t)$, the geminate recombination dynamics in the absence of the quencher in the system is known, then for the system with quencher the electron dynamics is determined by (5) and the

total radical population dynamics is determined by (8). As geminate recombination is a diffusion problem which needs numerical treatment, a general analytical form cannot be achieved for (5) and (8). However, the electron survival possibility $\Omega(t)$ can usually be empirically represented as a biphasic exponential decay. If we use the following bi-exponential to represent $\Omega(t)$,

$$\Omega(t) = Ae^{-k_1 t} + (1 - A)e^{-k_2 t}$$
(9)

then (5) and (8) can be rewritten analytically as

$$[e^{-}](t) = (1 - \eta)[Ae^{-(k_1 + k_q[Q])t} + (1 - A)e^{-(k_2 + k_q[Q])t}]$$
(10)

$$[R](t) = \eta + (1 - \eta) \left(\frac{(A(k_2 - k_1) + k_1 + k_q[Q])k_q[Q]}{(k_1 + k_q[Q])(k_2 + k_q[Q])} + \frac{Ak_1}{k_1 + k_q[Q]} e^{-(k_1 + k_q[Q])t} + \frac{(1 - A)k_2}{k_2 + k_q[Q]} e^{-(k_2 + k_q[Q])t} \right)$$

(11)

Note that the electron and the radical dynamics in the presence of scavenger can still be described by biphasic decays, but the radical population variation has a constant offset term. Figure A.1 shows an example of the geminate recombination dynamics of the radical and the electron, with and without electron quencher in the system. The parameters used are A = 0.514, $k_1 = 0.020 \text{ ps}^{-1}$, $k_2 = 0.345 \text{ ns}^{-1}$, [Q] = 0.2 M, $\eta = 0.59$, and $k_q = 0.021 \text{ ps}^{-1} \text{ M}^{-1}$.

Supporting Information References

1. A Unified Electron Transfer Model for the Different Precursors and Excited States of the Hydrated Electron, T. W. Kee, D. H. Son, P. Kambhampati, and P. F. Barbara, *J. Phys. Chem. A* **105**, 8434-39 (2001).

Figure S1: Population variation of the radical and the electron in a geminate recombination system. $\Omega(t)$ is identical population variation for the geminate partners in absence of electron quencher in the system. [R](t) and $[e^{-}](t)$ are the individual population variations for the radical and electron with electron scavenger in the system. See text for the parameters used.



Figure S2: Transient absorption traces at 52 (of the 332) probe wavelengths and their fits (dashed lines) resulting from global target analysis (with 3 different nitrate quencher concentrations) using the kinetic scheme from Figure 6(b). Probe wavelength indicated as ordinate label, the transient absorption unit is mOD. Note that the time axis is linear until 0.5 ps, and logarithmic thereafter. Key: black 0 M nitrate added, measured from 323-572 nm, red 0.2 M 292-572 nm, blue 0.5 M 292-572 nm, green 0 M 390-696 nm, magenta 0.2 M 390-696 nm, cyan 0.5 M 390-696 nm. Note that below 460 nm a coherent artifact at zero delay, which arise from two-photon absorption (2PA) of the solvent, was present. This was modeled as a sequence of three short lived components (\approx 10 fs). The Instrument Response Function (IRF) was described by a Gaussian with FWHM \approx 35 fs. The chirp in the white light continuum was described by a third order polynomial, and was \approx 300 fs over the full wavelength range. The average root mean square error of the fit was 0.11 mOD.





	<i>k_{relax}</i>	k_e'	k _e	Σk	
	0.68	0.19	0.027	0.027	
[KNO ₃]/mM	k _{e1}	k_{e2}	k _{e3}	k _{e4}	k _{e5}
0	0.044	0.071	0.011	0.0078	0.00017
200	0.94	0.43	0.021	0.060	0.0042
500	2.5	2.4	0.018	0.077	0.010
[KNO ₃]/mM	k_{R1}	k_{R2}	k_{R3}	<i>k</i> _{<i>R</i>4}	k_{R5}
0	0.044	0.071	0.011	0.0078	0.00017
200	0.032	0.056	0.0014	0.00043	0
500	0.066	0.091	0.011	0.0024	0

Table S1: Complete list of rate constants (in ps⁻¹) estimated from the global target analysis. Estimated relative error is 10%. See Figure 6 for the definition of the rate constants. The same k_{relax} , k_e' , k_e and Σk were used to fit the three datasets of different KNO₃ concentrations.

Table S2: Complete list of lifetimes (in ps) and relative amplitudes for the tri-exponential decays of R and *e* derived from Table S1.

	S_1 '	S_1	
	1.15	18.3	
[KNO ₃] / mM	$ au_{e1}$	$ au_{e2}$	$ au_{e3}$
0	8.4 (60%)	52 (16%)	6000 (24%)
200	0.73 (31%)	12.5 (51%)	241 (18%)
500	0.21 (49%)	10.5 (41%)	96 (10%)
[KNO ₃]/mM	$ au_{R1}$	$ au_{R2}$	$ au_{R3}$
0	8.4 (60%)	52 (16%)	6000 (24%)
200	11.4 (64%)	540 (8%)	inf (28%)
500	6.4 (58%)	74 (8%)	inf (34%)