Supporting Information for: Sub-Picosecond Production of Solute Radical Cations in THF after Radiolysis

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Section S1. Radiation chemistry details for aryl-bromide scavengers.

Lifetime of Br₂F[•]. Optical Fiber Single-Shot (OFSS) transient absorption following radiolysis of 300mM 9,9-Dihexyl-2,7-dibromofluorene (Br₂F) in THF at different wavelengths is shown in Figure S1.1 below. Aryl-halides, particularly bromides, are known to rapidly dissociate upon attaching an electron.¹ The lifetime of Br₂F radical anion is uncertain, but likely < 60 ps, and probably ~ 20 ps. A problem is that radical anion and cation spectra overlap, and it is not known where the radical anion might be clearly observed. 760nm is near the peak absorption for $Br_2F^{+\bullet}$; it is expected that part of the 60 ps decay is due to geminate recombination, and part to Br₂F[•] dissociation. Note that for unsubstituted biphenyl and fluorene, radical anions are known to have a peak absorption ~50 nm to the blue of the radical cations.² It is thus reasonable to expect that the faster 20 ps decay at 710nm is due more to Br₂F[•] dissociation than cations. We note however that there should be far more radical anions made than cations, so the smaller signal at 710 nm may the tail of the decay, with faster components unresolved, making the ~ 20 ps lifetime an upper limit for the lifetime of the radical anion. It also adds support to the idea that the signal at 760 nm is predominantly due to radical cations, even at short times. The longer time tail at both 710 and 760 nm is most certainly due to $Br_2F^{+\bullet}$ recombination alone.

Solvated electron absorption is not an important component at 710 or 760nm, as shown by the trace at 950nm where they absorb much more strongly.



<u>Figure S1.1</u>: Transient absorption of a 300mM Br2F solution in THF following radiolysis at 3 wavelengths, with fits labelled by the lifetime of the 1st decay component.

Summary of details for all aryl-bromides tested. Table S1.2 below gives determined spectral parameters for the the radical cations of four aryl-bromides tested as candidates as hole scavengers. Anion lifetimes were determined with fits to data such as the ones shown in Figure S1.1 for Br₂F. Note that in the previous work, we reported the lifetime of 4-bromobiphenyl radical anion as ~30 ps.¹ Here we find a shorter 13.9 ps lifetime, which is expected to be more accurate. The previous value was determined at 800 nm where the radical cation likely absorbs much more strongly than the radical anion,² giving a decay likely dominated by geminate recombination of the cation rather than radical anion dissociation. Despite the uncertainties in radical anion lifetimes, we find that they are well correlated with the computed barriers (B3LYP/6-31g(d)/THF) for dissociation to make Br- and an aryl radical, as seen in Figure S1.3 below. While the correlation is only 3 points, it gives some support to the assignment of the Br₂F-• lifetime being ~ 20 ps. In previous work we found a similar ~linear correlation previously for a wide range of aryl halides.¹

Experiments also sought to identify new spectral features in concentrated Br_2F solutions that might be attributed to dimer radical cations. Such species are known particularly for aromatics like benzene giving new absorptions to the red of the radical cation, but were expected to be unlikely with Br_2F due to the terminal bromine atoms and dihexyl side-chains. None were detected.

A possible concern was loss of bromine atoms after radiolysis, as these would have the ability to oxidize many solutes, particularly those with low ionization potentials. Computed dissociation energies for bromine atom loss from radical cations are given in Table S1.2 and are all large and positive, thus loss is very unlikely.

	λ_{\max}^{a} (nm)	$\epsilon (\mathrm{M}^{-1}\mathrm{cm}^{-1})^b$	$\frac{\Delta G(Br^{\bullet})}{(eV)^{c}}$	Anion Lifetime	$\frac{\Delta E_{\text{barrier}}}{(\text{meV})^{d}}$
9,9-Dihexyl-2,7-dibromofluorene	775	22600	3.63	19.9	14.8
(Br ₂ F)					
4-bromobiphenyl	760	17800	3.51	13.9	1.7
4,4-Bis(bromomethyl)biphenyl	760	16000	1.08		23.7
2,7-Bis(bromomethyl)-9,9-dihexyl-	710	21400	1.13	23.4	26.1
9H-fluorene					

Table S1.2: Summary of	aryl-bromide	sample parameters
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^{*a*} Radical cation absorption spectrum maximum. ^{*b*} Peak radical cation extinction coefficient determined in 1,2-dichloroethane relative to biphenyl as described previously. ^{*c*} Computed free energy for loss of a bromine atom from the radical cation (B3LYP/6-31G(d)). ^{*d*} Computed radical anion dissociation barrier.



<u>Figure S1.3</u>: Computed radical anion dissociation barriers, B3LYP/6-31+G*/SCRF=THF. Computed barrier heights are well correlated with measured radical anion lifetimes.

Section S2. Spectral details for $Br_2F^{+\bullet}$.

The absorption spectrum of 1 M 9,9-dihexyl-2,7-dibromofluorene (Br₂F) in THF following pulse radiolysis at various delay times is shown in Figure S2.1 below. The spectrum was unchanged when 0.5 M dichloromethane was added. Data were recorded with ~1 ns time resolution in transient digitizer based experiments where collection of high quality spectra is best. The band peaking at ~775 nm is the radical cation of Br₂F, maximized at the earliest times and decreasing at later times. There are 2 other apparent peaks. The peak at ~415 nm is due to a combination of Br₂F⁺⁺ and ³Br₂F* formed by recombination. This peak grows from 1 to 2 ns, then decays. At long times this peak appears to blue-shift slightly, when triplets dominate the band. Kinetic modeling at 770 and 420 nm assuming all recombinations of Br₂F⁺⁺ and Br⁻ make Br₂F*, and further all singlets become triplets rapidly suggesting that Br₂F⁺⁺ absorption at 1 ns is at least 2.55x larger at 420 nm than 770 nm; at most 22% of the 1ns peak at 420 nm is due to ³Br₂F* absorption. At long times, >> 100 ns, a 3rd band peaking at 540 nm grows in. This band is attributable to complexes of Br atoms made during recombination with the aromatic rings of Br₂F, similar to those described for similar Cl atom complexes described by Bird.³



Figure S2.1: Absorption spectra at various delay times following radiolysis of a Br₂F solution.

Section S3. Determination of the $Br_2F^{+\bullet}$ extinction coefficient.

The extinction coefficient of the radical cation was determined by comparison of the absorbance after radiolysis of a 10 mM Br₂F solution in 1,2-dichloroethane (DCE) to a 10 mM sample of biphenyl (BP) in DCE. In DCE, radiolysis produces DCE^{+•} which transfers the positive charge to solutes to make identical concentrations of BP^{+•} and Br₂F^{+•}, but no anions because DCE^{-•} dissociates rapidly. Data shown below are averages of 3 experiments, each composed of 4 electron pulse shots for consistency. Using the ratio of absorbances and Gould's $\varepsilon = 14500 \text{ M}^{-1}\text{cm}^{-1}$ for BP^{+•},^{4,5} we determined $\varepsilon = 21085 \pm 10\% \text{ M}^{-1}\text{cm}^{-1}$ for Br₂F^{+•}.



<u>Figure S3.1</u>: Pulse radiolysis data from samples containing either Br_2F or biphenyl in 1,2-dichloroethane.

Section S4. Impact of absorptions from solvated electron and Br_2F^{-} at low [Br_2F], and their mitigation by adding 0.5 M diboromomethane.

Here we discuss the fate of electrons from ionizations in solutions with Br_2F in THF. Transient absorption data at 950 nm following radiolysis for low concentrations of Br2F in THF without CH2Br2 (Ar saturated) are shown in Figure S4.1. At 950 nm, solvated electrons absorb more strongly than at 770 nm. At the same time, the extinction coefficient of $Br_2F^{+\bullet}$ is only 15% of the value at 770 nm, which coupled with the low $Br_2F^{+\bullet}$ yield, allows solvated electron absorption to dominate the signal.



Figure S4.1: Transient absorption at 950 nm

Initial fits were produced by fitting all of the data shown simultaneously to a model that includes a 3 exponential decay to describe the range of geminate recombination distances and rates, pre-solvated electron capture, and an electron attachment rate. These fits gave a rather large electron attachment rate of $k_{att} = 1.3e11 \text{ M}^{-1}\text{s}^{-1}$, with a pre-solvated electron quenching coefficient $q = 14.3 \text{ M}^{-1}$ (Abs(t=0) ~ e^{-q*c}, c=concentration). Fits shown in Figure S4.1 were improved slightly by including a Smoluchowski time-dependent rate term,^{6,7} giving a more reasonable $k_{att} = 5.4e10 \text{ M}^{-1}\text{s}^{-1}$, and $q = 11.8 \text{ M}^{-1}$. This rate of solvated electron attachment is well within the range of others reported in THF by Kadhum.⁸ We further note that the initial fit without the time-dependent term is among or greater than the very highest rates, thus likely suspect. The quenching coefficient gives a pre-solvated scavenging C₃₇ value, at which 37% of electrons survive capture, of C₃₇ = 1/q = 85 mM, which is consistent with that reported by Saeki for biphenyl in THF, 87 mM,⁹ with the q determined with a time-dependent rate being nearly the same.

Note that even at 50 mM Br_2F , there are still surviving solvated electrons with a lifetime near 110 ps. At 770 nm the electron extinction coefficient is weak compared to $Br_2F^{+\bullet}$, but there are many more of them than radical cations and contribute a noticeable fast decay to all of the data. These electrons are captured to make $Br_2F^{-\bullet}$. Despite the fact that this species is short lived, it gives an addition absorption that grows on the same timescale as the electron decay followed by a complex decay. The extra absorptions and complex time-dependence due to solvated electrons and $Br_2F^{-\bullet}$ make interpreting the data at 770 nm much more difficult and uncertain. Figure S4.2 below gives data without dibromomethane that can be compared to Figure 2 in the main manuscript that includes it.



Figure S4.2: Pulse radiolysis data for Br₂F solutions that do not contain CH₂Br₂.

To remove the extra complexity in analysis, experiments described in the manuscript included 0.5 M dibromomethane, to remove solvated electron and complex Br_2F^{\bullet} absorptions from the signals. We note that not only is CH_2Br_2 effective at removing solvated electrons and thus Br_2F^{\bullet} , we find that it may also be a very good pre-solvated electron scavenger, removing electrons on a sub-10 ps timescale. Figure S4.3 demonstrates that 0.5 M reduced solvated electrons by at least an order of magnitude. The lack of a decay in the remainder indicates a different species than solvated electrons – this is likely a very weak absorption of a THF radical, likely the one produced after the 0.5 ps proton transfer from THF^{+•} to a neighboring THF molecule. Thus the data below suggests that there is essentially no solvated electrons left in the presence of 0.5 M CH_2Br_2 , even at times as early as 10-15 ps, and there is not evidence for the predicted 25 ps decay due to e- reacting with CH_2Br_2 . While it is possible this is simply due to an underestimated rate with e- or time-dependent rates of reaction, it seems plausible that scavenging of e- prior to solvation is also important.



Figure S4.3: Essentially complete quenching of solvated electrons in THF by CH₂Br₂.

Section S5. Comparison of data from different time-resolution experiments, at room temperature.

In Figure S5.1 below, we compare ~ 1 ns resolution photodiode/transient digitizer data and 10-15 ps resolution OFSS data, with fits extrapolated to show the intercept at t=0. Note that fit shown for the OFSS data has had the fast component due to Br₂F^{-•} subtracted out. Fits with digitizer data give a 37% smaller t=0 value of the absorbance, due to recombination that occurs on faster timescales than the digitizer experiment is sensitive to.



<u>Figure S5.1</u>: Comparison of data and fits to obtain t=0 absorbance due to Br2F from experiments with different time resolution: OFSS (15 ps), digitizer (\sim 1 ns).

Section S6. Impact of side chains on $Br_2F^{+\bullet}$ production.

In Figure S6.1 below, we show data from 500 mM samples of Br₂F and a version missing the hexyl side chains, 2,7-dibromofluorene. 500 mM was near the limit of solubility for dibromofluorene. This molecule has 96 fewer electrons (38%) than Br₂F with 252 electrons/molecule, so we expect that the direct ionization yield in dibromofluorene ($G_{dir} * f_e^{Br_2F}$) would be 38% smaller than in Br₂F if all ionizations in the hexyl chains transfer to the Br₂F aromatic core. This gives a prediction of a 20-27% smaller observed yield for dibromofluorene, assuming G_{dir} has a range of 3-4 / 100eV.

Data were fit in the same way as all Br_2F samples, ignoring the fast ~25 ps component. From the fits below, the t=0 yield decreases by 19.2%. Being slightly smaller than predicted may imply that a small number of ionizations on the hexyl chains do not make it to the core, but rather transfer to THF. Note that the alkyl chains will NOT have an antenna effect in THF, as it is uphill in energy to transfer a hole from THF to a hexyl chain by ~ 0.7 eV (dft, b3lyp/6-31+g*, scrf=thf).



Figure S6.1: Comparison of pulse radiolysis data of samples containing hole scavengers with and without dihexyl side chains.

Section S7: Complimentary experiments using biphenyl (BP) as a hole scavenger in place of Br_2F .

The computed driving force for the hole transfer from THF⁺⁺ to BP is $\Delta E = -0.90$ eV, only slightly less than for Br₂F, -1.06 eV (B3LYP/6-31+G*/SCRF=THF). BP is a good comparison because it lacks the Br atoms and hexyl side chains that Br₂F has. It thus produced a much lower direct ionization yield, about 1/3 of that of Br₂F. On the other hand, these experiments are more complex to interpret as both radical cations and anions are formed and are long lived and absorb at 700nm. We note that radical cations prepared in low temperature glasses appear to have a stronger absorbance at 700nm, with radical anions shifted to the blue by ~ 50nm.² At room temperature these spectra broaden and may make both species with more similar absorption coefficients. We determined that CH₂Br₂ reacts with BP⁻⁺ at 1.1e10 M⁻¹s⁻¹ in a low concentration BP solution. This is responsible for the ~ 125 ps decay in the data in the traces in Figure S7.1 below.



<u>Figure S7.1</u>: 0.5 M CH₂Br₂ removes the excess electron from BP-• on a ~125 ps timescale, exposing absorptions due to BP+•.

This data was fit in the same manner as Br_2F data in the manuscript, holding the decay rate due to the reaction of CH_2Br_2 with BP^{-*} constant. The remainder of the signal is due to BP^{+*} . Given that anions obscure the signal at short times, the extrapolation of the BP^{+*} signal to t=0 is less sure than with Br_2F , and may miss faster transients.

If we compare the difference of the observed yield and direct yield (G_{obs} - G_{dir}) with both BP and Br₂F scavengers (with and without side-chains included in the direct yield), we obtain the results in Figure S7.2 below. These graphs show that the scavenger radical cation yield produced by transfer from THF⁺⁺ is remarkably similar in Br₂F and BP, as one might expect for these similar molecules. Note that if side chains are not included in the direct ionization yield of Br₂F, the comparison is poor, supporting including them in them analysis for Br₂F. The graphs also suggest that the direct ionization yield of the 2 solutes is between 3 and 4/100eV, as BP with G_{dir} = 3 lies a bit below Br₂F, while with G_{dir} = 4 lies a bit above.



<u>Figure S7.2</u>: Comparison of the difference in the observed radical cation yield and direct solute ionization yield (G_{obs} - G_{dir}) for Br₂F and BP solutes in THF with 0.5 M CH₂Br₂.

Section S8. Table of Electron densities of each component in samples. * All samples contain 0.5 M CH₂Br₂: 78 e-/molecule, = 0.039 mol e-/cm³ in samples THF: 40 e-/molecule Br₂F (including side-chains): 252 e-/molecule f_e = fraction of total electron density

$[Br_2F]$	Density	[THF]	Br ₂ F mol	THF mol	Br ₂ F	THF	CH_2Br_2
(mol/dm^3)	(g/cm^3)	(mol/dm^3)	e-/cm ³	e-/cm ³	$f_{\rm e}$	$f_{\rm e}$	fe
0	0.933	11.727	0.000	0.469	0.000	0.923	0.077
5	0.933	11.701	0.001	0.468	0.002	0.921	0.077
10	0.934	11.676	0.003	0.467	0.005	0.918	0.077
25	0.936	11.601	0.006	0.464	0.012	0.911	0.077
50	0.939	11.475	0.013	0.459	0.025	0.899	0.076
100	0.946	11.224	0.025	0.449	0.049	0.875	0.076
200	0.959	10.722	0.050	0.429	0.097	0.827	0.075
300	0.972	10.219	0.076	0.409	0.144	0.781	0.075
500	0.998	9.214	0.126	0.369	0.236	0.691	0.073
750	1.030	7.958	0.189	0.318	0.346	0.583	0.071
1000	1.063	6.701	0.252	0.268	0.451	0.479	0.070

In the manuscript we treat the THF and CH_2Br_2 together as the solvent, summing their fractions of the electron density. We note that holes from CH_2Br_2 have a chance to be captured by Br_2F , but because $[Br_2F] \ll [THF]$ most holes likely transfer to THF first, then are possible to be captured by Br_2F as described in the paper. The fraction of the sample electron density due CH_2Br_2 is less than 8% for all samples, so any errors from the approach are likely small.

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