Lifetime of Triplet Photosensitizers in Aerosol Using Time-Resolved Photoelectric Activity

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Supporting Information

13 pages, 8 tables

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Estimating Particle Phase Concentrations

We estimate the concentration of solutes as a function of RH in these predominantly NaCl aerosol particles using the E-AIM Model III.[1-2] As a first estimate, we carry out the calculation with only NaCl, using the option to suppress the formation of NaCl(s) in the supersaturated regime (<75% RH). The concentration of the photosensitizer is less than 1% of the concentration of chloride, so the associated error is less than that which arises from uncertainty in our measured RH. The latter uncertainty, ±2%, leads to an approximately 5 to 15% error in the concentration of solute, depending on the RH. To calculate the concentration of photosensitizer, we scale the NaCl concentration by the photosensitizer to NaCl ratio in the atomizer solution. For example, at 65% RH, the NaCl concentration is 8.3 mol/kg and the model-calculated density is 1.25 g/cm^3. Using these values, the NaCl molarity is 7.0 mol/L. For a typical solution, where the photosensitizer:NaCl mole ratio is 0.01, the concentration of photosensitizer is 0.070 mol/L.

Repeating this approach with species that are included in the E-AIM model, such as nitrate, results in discrepancies of approximately 5% between the estimate and the model-calculated value for the relatively small concentrations in this study. For an aqueous aerosol with composition (NaCl:$NaNO_3$ = 100:1), E-AIM predicts [NO_3^-] = 0.074 mol/L. The approximate procedure outlined above, for which the identity of the solute does not matter, yields a value of 0.070 mol/L.

Description of DFT Calculations

We used the Gaussian 16[3] software to carry out DFT calculations. We first optimized geometries and calculated vibrational frequencies and thermochemical data at the B3LYP/6-311G(d) level of theory. We calculated single point electronic energies with this optimized geometry at the B3LYP/6-311++G(2df,2p) level of theory both for isolated molecules and using

the SMD[4] implicit solvent model with the solvent set to water. We used empirical dispersion corrections (GD3[5]) at both stages of the calculation.

In the tables that follow, E_0 is the electronic energy, ZPE is the zero-point energy, ΔE_{therm} is the thermal correction to the energy, ΔH_{therm} is the thermal correction to the enthalpy, and ΔG_{therm} is the thermal correction to the free energy. All the thermal corrections assume a temperature of 298 K. The electron binding energies shown in Figure 2 of the main article and tabulated in Table S8 are the adiabatic ionization energies at 0 K for each species, calculated as the difference in E_0(water) + ZPE for IC and IC^+ or AQ2S and AQ2S-neutral radical.

3. DFT Results

IC (S_0)

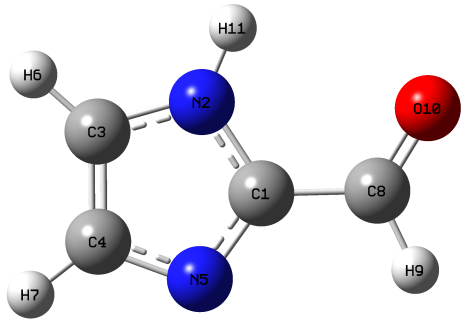

Table S1. Calculated geometry and thermochemistry for IC (S_0)

	Coordinates (standard orientation)			Thermochemistry	
Center	X	Y	Z		Energy / Hartree
C1	-0.233570	-0.278671	-0.000014	E_0(gas)	-339.672918479
N2	0.295938	0.983623	0.000086	E_0(water)	-339.688190740
C3	1.652930	0.855158	-0.000138	ZPE	0.080685
C4	1.892780	-0.507026	-0.000180	ΔE_{therm}	0.086171
N5	0.719580	-1.198946	-0.000073	ΔH_{therm}	0.087116
H6	2.316214	1.704221	-0.000204	ΔG_{therm}	0.051333
H7	2.848171	-1.008452	-0.000277		
C8	-1.674517	-0.507240	0.000030		
H9	-1.964198	-1.573556	0.000023		
O10	-2.484949	0.397781	0.000240		
H11	-0.254954	1.829479	0.000264		

IC (T_1)

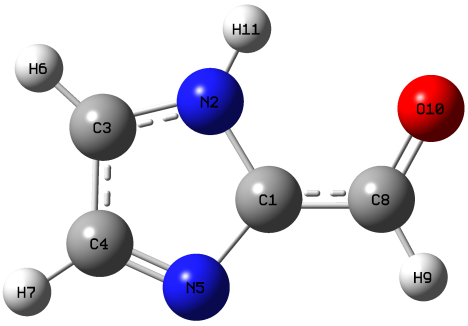

Table S2. Calculated geometry and thermochemistry for IC (T_1)

	Coordinates (standard orientation)			Thermochemistry	
Center	X	Y	Z		Energy / Hartree
C1	-0.265474	-0.326166	-0.000066	E_0(gas)	-339.565743724
N2	0.226253	0.997325	-0.000268	E_0(water)	-339.586346180
C3	1.590563	0.926914	-0.000048	ZPE	0.075695
C4	1.890346	-0.478451	-0.000087	ΔE_{therm}	0.081284
N5	0.816771	-1.229294	-0.000179	ΔH_{therm}	0.082229
H6	2.235007	1.790220	-0.000023	ΔG_{therm}	0.045360
H7	2.886113	-0.903594	-0.000171		
C8	-1.635142	-0.579592	0.000356		
H9	-1.971032	-1.620728	0.000092		
O10	-2.443529	0.412935	0.000235		
H11	-0.265474	-0.326166	-0.000066		

IC^+

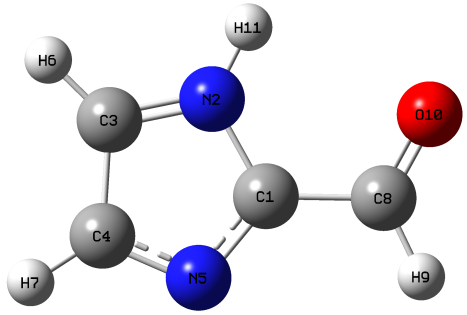

Table S3. Calculated geometry and thermochemistry for IC^+

	Coordinates (standard orientation)			Thermochemistry	
Center	X	Y	Z		Energy / Hartree
C1	-0.227388	-0.315670	0.000022	E_0(gas)	-339.337274989
N2	0.273853	0.993337	0.000134	E_0(water)	-339.448858958
C3	1.593964	0.913534	-0.000214	ZPE	0.078896
C4	1.888381	-0.521236	-0.000186	ΔE_{therm}	0.084686
N5	0.760012	-1.215810	-0.000039	ΔH_{therm}	0.085631
H6	2.253219	1.771261	-0.000313	ΔG_{therm}	0.048452
H7	2.869635	-0.977472	-0.000319		
C8	-1.696627	-0.546601	0.000240		
H9	-2.028552	-1.593791	-0.000170		
O10	-2.421244	0.418812	0.000082		
H11	-0.311385	1.826663	0.000313		

IC dimer #1

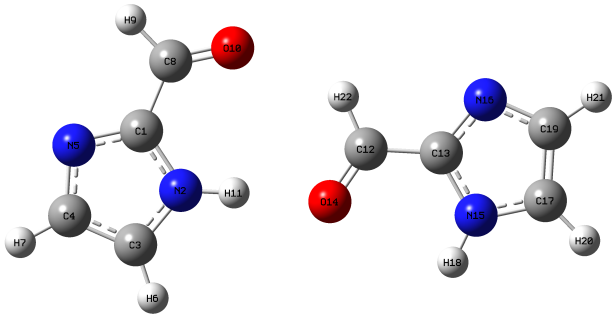

Table S4. Calculated geometry and thermochemistry for IC dimer #1

	Coordinates (standard orientation)			Thermochemistry	
Center	X	Y	Z		Energy / Hartree
C1	-3.057764	0.501913	0.000267	E_0(gas)	-679.361971
N2	-2.304449	-0.640621	-0.001201	E_0(water)	-679.384749
C3	-3.172403	-1.685994	0.000568	ZPE	0.162943
C4	-4.441092	-1.127747	0.002930	ΔE_{therm}	0.175688
N5	-4.359557	0.227484	0.002899	ΔH_{therm}	0.176632
H6	-2.838194	-2.710673	0.000014	ΔG_{therm}	0.120300
H7	-5.390294	-1.641399	0.004747		
C8	-2.496253	1.842802	-0.001111		
H9	-3.264958	2.637028	0.000902		
O10	-1.304924	2.095114	-0.004119		
H11	-1.279496	-0.688893	-0.002854		
C12	1.261969	0.153900	-0.000469		
C13	2.709915	0.078426	0.000473		
O14	0.565468	-0.856613	-0.003504		
N15	3.379672	-1.117703	-0.002025		
N16	3.556252	1.099842	0.003681		
C17	4.711095	-0.837154	-0.000229		
H18	2.931640	-2.022137	-0.004637		
C19	4.796729	0.545441	0.003217		
H20	5.466038	-1.606003	-0.001540		
H21	5.689992	1.150523	0.005397		
H22	0.824324	1.161017	0.001598		

IC dimer #2

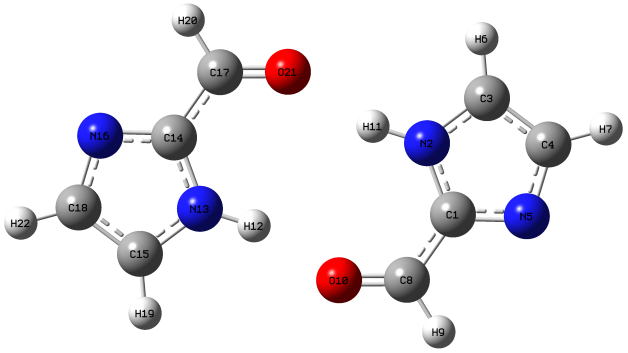

Table S5. Calculated geometry and thermochemistry for IC dimer #1

	Coordinates (standard orientation)			Thermochemistry	
Center	X	Y	Z		Energy / Hartree
C1	2.5181830	-0.6953720	-0.0002520	E_0(gas)	-679.372993
N2	2.0502750	0.5922320	-0.0005570	E_0(water)	-679.388985
C3	3.1331650	1.4062580	-0.0005640	ZPE	0.163448
C4	4.2420160	0.5690510	-0.0000700	ΔE_{therm}	0.175855
N5	3.8514180	-0.7268540	-0.0000200	ΔH_{therm}	0.176799
H6	3.0397510	2.4799410	-0.0008430	ΔG_{therm}	0.122110
H7	5.2835830	0.8512870	0.0000970		
C8	1.6869210	-1.8752470	-0.0001950		
H9	2.2632210	-2.8152050	-0.0000490		
O10	0.4620990	-1.8833890	-0.0004940		
H11	1.0730890	0.8988230	-0.0008390		
H12	-1.0735420	-0.8991380	0.0000010		
N13	-2.0505970	-0.5923350	0.0003320		
C14	-2.5180860	0.6954730	0.0002690		
C15	-3.1337370	-1.4059820	0.0007130		
N16	-3.8512920	0.7273470	0.0009490		
C17	-1.6864250	1.8749770	-0.0003250		
C18	-4.2423200	-0.5684080	0.0010940		
H19	-3.0407310	-2.4797070	0.0007340		
H20	-2.2623360	2.8151840	-0.0001120		
O21	-0.4615980	1.8823700	-0.0006900		
H22	-5.2839830	-0.8502600	0.0015350		

AQS (S_0)

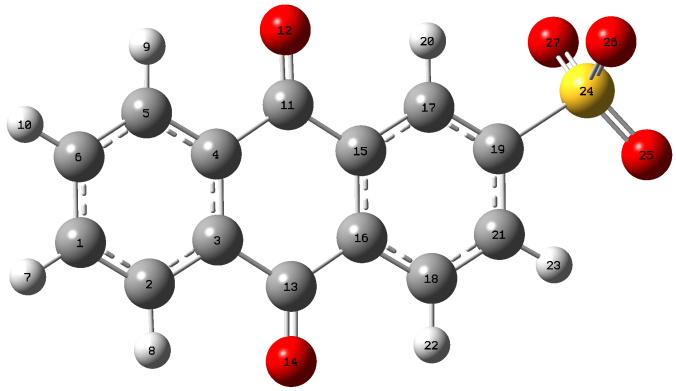

Table S6. Calculated geometry and thermochemistry for AQS (S_0)

	Coordinates (standard orientation)			Thermochemistry	
Center	X	Y	Z		Energy / Hartree
C1	5.593225	-0.315378	0.050308	E_0(gas)	-1312.471478
C2	4.662981	0.716167	0.065260	E_0(water)	-1312.569121
C3	3.294500	0.432374	0.029152	ZPE	0.181807
C4	2.862427	-0.901478	-0.022378	ΔE_{therm}	0.197153
C6	3.804589	-1.933997	-0.037122	ΔH_{therm}	0.198097
C6	5.162781	-1.644268	-0.001031	ΔG_{therm}	0.135871
H7	6.654809	-0.088531	0.078531		
H8	4.967994	1.755489	0.104794		
H9	3.442417	-2.954771	-0.077170		
H10	5.889461	-2.451060	-0.012744		
C11	1.403336	-1.248502	-0.062301		
O12	1.053935	-2.417137	-0.106817		
C13	2.315065	1.566111	0.046426		
O14	2.714579	2.722494	0.091627		
C15	0.435054	-0.122965	-0.045143		
C16	0.877838	1.220856	0.006927		
C17	-0.930904	-0.402262	-0.081109		
C18	-0.069195	2.248420	0.021383		
C19	-1.865120	0.633860	-0.066153		
H20	-1.260858	-1.433136	-0.120808		
C21	-1.428460	1.958572	-0.014800		
H22	0.284479	3.272639	0.061411		
H23	-2.178198	2.741295	-0.004318		
S24	-3.653715	0.247678	-0.114045		
O25	-4.306188	1.576278	-0.083219		
O26	-3.853350	-0.571853	1.101585		
O27	-3.804320	-0.489994	-1.387782		

AQS (T_1)

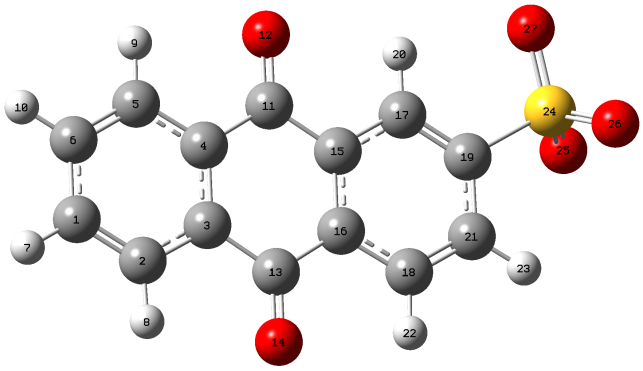

Table S7. Calculated geometry and thermochemistry for AQS (T_1)

	Coordinates (standard orientation)			Thermochemistry	
Center	X	Y	Z		Energy / Hartree
C1	5.254372	0.041617	0.002657	E_0(gas)	-1312.388052
C2	4.231897	0.968140	0.001049	E_0(water)	-1312.470290
C3	2.882109	0.563623	-0.000388	ZPE	0.177280
C4	2.580519	-0.822440	0.000905	ΔE_{therm}	0.193018
C6	3.641198	-1.758155	0.001497	ΔH_{therm}	0.193962
C6	4.953247	-1.336670	0.002674	ΔG_{therm}	0.131726
H7	6.289527	0.371447	0.003703		
H8	4.428548	2.034748	0.000055		
H9	3.388363	-2.812658	0.001492		
H10	5.757132	-2.067757	0.003766		
C11	1.203557	-1.298088	0.001480		
O12	0.938048	-2.533966	-0.004095		
C13	1.831362	1.589624	-0.004693		
O14	2.098107	2.806500	-0.006532		
C15	0.150292	-0.293245	0.000701		
C16	0.451695	1.092763	-0.002804		
C17	-1.201651	-0.710667	-0.000466		
C18	-0.610658	2.021581	0.001188		
C19	-2.209473	0.224494	-0.001219		
H20	-1.428144	-1.769434	0.000879		
C21	-1.923281	1.608385	0.000773		
H22	-0.350606	3.074230	0.002771		
H23	-2.733275	2.328606	0.005066		
S24	-3.929019	-0.297995	0.003012		
O25	-4.539510	0.234229	-1.245105		
O26	-4.545744	0.307085	1.211111		
O27	-3.938194	-1.780978	0.033865		

AQS-neutral radical

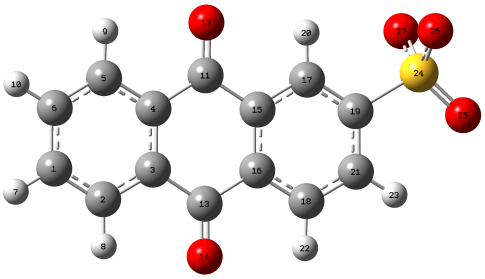

Table S7. Calculated geometry and thermochemistry for AQS-neutral

	Coordinates (standard orientation)			Thermochemistry	
Center	X	Y	Z		Energy / Hartree
C1	5.267447	0.013787	-0.000389	E_0(gas)	-1312.295057
C2	4.248635	0.958294	-0.000200	E_0(water)	-1312.311133
C3	2.911842	0.549239	0.000008	ZPE	0.180670
C4	2.602769	-0.823765	0.000056	ΔE_{therm}	0.196395
C6	3.634935	-1.766252	-0.000107	ΔH_{therm}	0.197339
C6	4.960357	-1.349555	-0.000345	ΔG_{therm}	0.135095
H7	6.303133	0.336519	-0.000570		
H8	4.464189	2.020123	-0.000205		
H9	3.374324	-2.817929	-0.000036		
H10	5.757668	-2.085140	-0.000496		
C11	1.192564	-1.301987	0.000305		
O12	0.914340	-2.486872	0.000566		
C13	1.843034	1.585449	0.000184		
O14	2.099812	2.775588	0.000361		
C15	0.116351	-0.261543	0.000182		
C16	0.421987	1.109669	0.000119		
C17	-1.214483	-0.677736	0.000145		
C18	-0.605428	2.055868	0.000003		
C19	-2.219763	0.282315	0.000006		
H20	-1.431589	-1.739216	0.000224		
C21	-1.933218	1.649111	-0.000046		
H22	-0.343336	3.106888	-0.000011		
H23	-2.740515	2.370920	-0.000157		
S24	-3.927436	-0.248675	-0.000123		
O25	-4.774050	0.932086	-0.000145		
O26	-4.114334	-1.194839	1.154645		
O27	-4.114153	-1.194805	-1.154965		

Table S8. Electron binding energies

Species	E_0(water)+ZPE (Hartree)	(E_0(water)+ZPE) IC^+ or AQ2S-neutral rad. (Hartree)	IP/Hartree	IP/eV
IC (S_0)	-339.6881907	-339.44886	0.238	6.46
IC (T_1)	-339.58635	-339.44886	0.141	3.83
AQ2S (S_0)	-1312.5691	-1312.3111	0.257	6.99
AQ2S (T_1)	-1312.4703	-1312.3111	0.1623	4.42

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