Free Energies of Proton-Coupled Electron Transfer Reagents and Their Applications

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1 General Considerations

Reagents were purchased from Sigma-Aldrich or Alfa Aesar. TEMPO$^•$ and 4-oxo-TEMPO$^•$ were sublimated under vacuum prior to use. TEMPO-H was prepared as reported previously.[1] Hexanes (mixture of isomers, HPLC grade) were purchased from Sigma-Aldrich and dispensed from an Argon-atmosphere solvent system with alumina drying columns. All reactions were performed in a nitrogen-filled glovebox (working O_2 level < 5 ppm). UV–Vis spectra were collected on an Agilent Cary 60 UV–Vis or Agilent Cary 5000 UV–Vis–NIR spectrophotometer inside of a nitrogen-filled glovebox.

2 UV-Vis characterization of 4-oxo-TEMPO$^•$ and TEMPO$^•$

2.1 *UV–Vis spectra of pure reagents*

Individual UV–Vis spectra were taken of 4-oxo-TEMPO$^•$ (oxo$^•$, λ_{max}= 459 nm), TEMPO$^•$ (λ_{max}= 473 nm), and TEMPO-H in hexane. The spectra were normalized to a concentration of 40 mM and are shown overlaid in Figure S1. TEMPO-H displayed a negligible UV–Vis trace, confirming it was free from TEMPO$^•$ contamination.

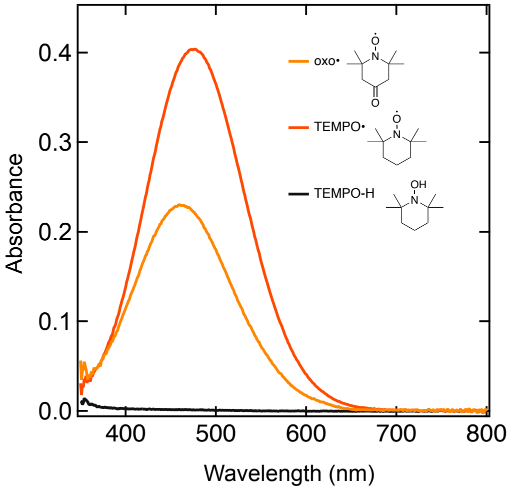


Figure S1. UV–Vis spectra of 40 mM oxo$^•$, TEMPO$^•$, and TEMPO-H in hexane.

2.2 *Molar absorptivities (ε) of 4-oxo-TEMPO$^•$ and TEMPO$^•$*

Beer's law plots were constructed for oxo$^•$ (Figure S2a) and TEMPO$^•$ (Figure S2b) in hexane. The molar absorptivities were determined to be ε_{459nm} = 5.86 M^{-1} cm^{-1} and ε_{473nm} = 10.27 M^{-1} cm^{-1} for oxo$^•$ and TEMPO$^•$, respectively. These values were in good agreement with the experimental values for $\varepsilon_{\lambda max}$ when ε was calculated at each wavelength (Figure S2c).

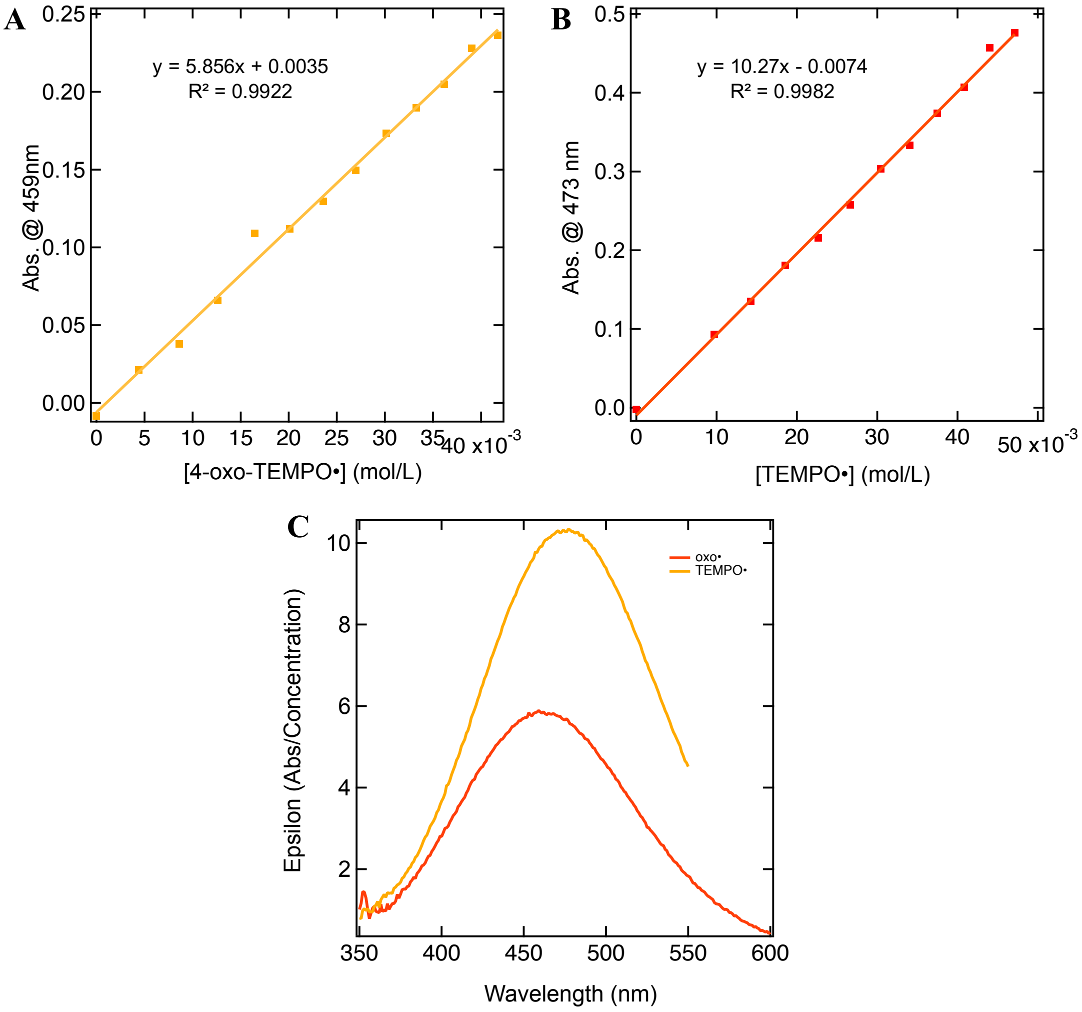
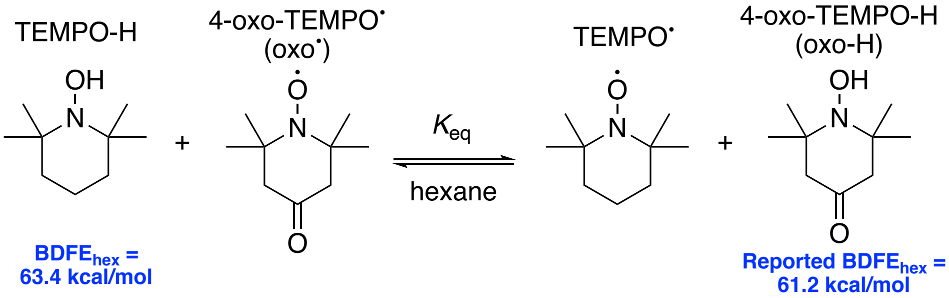


Figure S2. Concentration was plotted against absorbance at the λ_{max} for (**A**) oxo$^{\bullet}$ and (**B**) TEMPO$^{\bullet}$ in hexane. The slope of the resulting line is equal to $\varepsilon_{\lambda max}$ for each species. (**C**) The absorbance at each wavelength was divided by concentration of the sample to provide the epsilon at each wavelength.

3 UV–Vis Equilibration

Scheme 1. Reaction between TEMPO-H and oxo•. K_{eq} of this reaction is directly related to the relative bond strength of TEMPO-H and oxo-H.



The pseudo-self exchange reaction between 4-oxo-TEMPO• (oxo•) and TEMPO-H (Scheme 1) was analyzed to determine the bond dissociation free energy (BDFE) of 4-oxo-TEMPO-H (oxo-H) in hexanes. The equilibrium constant for this reaction, K_{eq}, gives the free energy of the reaction, $\Delta G°$. This free energy relates the BDFEs of the H-atom donor, TEMPO-H, and the H-atom receptor, oxo• (eq X–H + Y → X + Y–H $\Delta G° = \mathrm{BDFE(XH)} - \mathrm{BDFE(YH)}$ (S1). Utilizing the known TEMPO-H BDFE$_{hexane}$[2] = 63.4 kcal mol^{-1}, we were able to calculate the BDFE of oxo-H.

$$\mathrm{X{-}H + Y \rightarrow X + Y{-}H} \qquad \Delta G° = \mathrm{BDFE(XH)} - \mathrm{BDFE(YH)} \qquad \text{(S1)}$$

A range of experimental initial concentrations were chosen for the equilibration reaction, ranging from 1:0.33 – 1:1.2 oxo•:TEMPO-H (Table S1). A 2mL solution of 30 mM oxo• in hexanes was prepared in a quartz cuvette equipped with a stir bar. TEMPO-H stock solution in hexane (0.1933 M) was titrated incrementally across the range of oxo•:TEMPO-H molar ratios. After each TEMPO-H addition, the reaction was equilibrated with stirring for 20 min until the UV–Vis trace was constant. Sequential addition of TEMPO-H stock solution and subsequent equilibration resulted in seven experimental equilibrations with UV–Vis spectra shown in Figure S3. Addition of TEMPO-H resulted in a slight red shift in λ_{max} and an increase in absorbance as more TEMPO• was formed at equilibrium.

Table S1. Experimental setup for seven equilibration reactions between oxo$^{\bullet}$ and TEMPO-H. A solution of oxo$^{\bullet}$ (0.817 mL, 0.0734 M) was reacted with increasing amounts of TEMPO-H stock solution and equilibrated for 20 min. [oxo$^{\bullet}$]$_i$ and [TEMPO-H]$_i$ are initial concentrations of these species in solution.

Sample	oxo$^{\bullet}$ equiv.	TEMPOH equiv.	mmol oxo$^{\bullet}$	mmol TEMPOH	Total volume (mL)	[oxo$^{\bullet}$]$_i$ (mol/L)	[TEMPOH]$_i$ (mol/L)
A	1.0	0.33	0.060	0.020	2.103	0.0285	0.0095
B	1.0	0.50	0.060	0.030	2.289	0.0262	0.0131
C	1.0	0.63	0.060	0.038	2.328	0.0258	0.0161
D	1.0	0.71	0.060	0.043	2.356	0.0255	0.0182
E	1.0	0.83	0.060	0.050	2.393	0.0251	0.0209
F	1.0	1.0	0.060	0.060	2.444	0.0245	0.0245
G	1.0	1.2	0.060	0.072	2.506	0.0239	0.0287

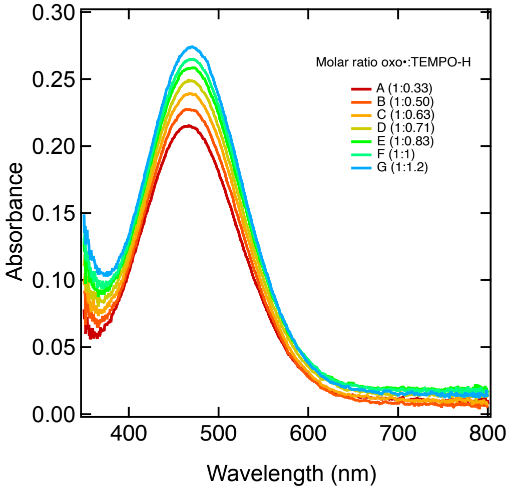


Figure S3. UV–Vis absorbances of oxo$^{\bullet}$ + TEMPO-H reactions corrected against a hexane blank.

4 Calculation of 4-oxo-TEMPO-H BDFE$_{hex}$

The concentrations of each species – oxo$^{\bullet}$, oxo-H, TEMPO$^{\bullet}$, and TEMPO-H – can be calculated at equilibrium using the total absorbance, the molar absorptivities of the two colored species (oxo$^{\bullet}$ and TEMPO$^{\bullet}$), and the initial concentrations of oxo$^{\bullet}$ and TEMPO-H. The total absorbance at each wavelength is the sum of the absorbance of each species (eq. S2). Mass balance dictates that the sum of the concentrations of related species (oxo$^{\bullet}$ + oxo-H; TEMPO$^{\bullet}$ + TEMPO-H) at equilibrium must be equal the initial concentration of the related reactant species (eqs. S3 and S4). Additionally, the concentration of the products oxo-H and TEMPO• must be equivalent (eq. S5) in the absence of decomposition or side reactivity (of which none was observed by NMR or UV–Vis spectroscopies).

$$\mathrm{Abs}^{\lambda} = l(\varepsilon^{\lambda}_{\mathrm{TEMPO}\bullet}[\mathrm{TEMPO}^{\bullet}] + \varepsilon^{\lambda}_{\mathrm{oxo}\bullet}[\mathrm{oxo}\bullet]) \tag{S2}$$

$$[\mathrm{oxo}^{\bullet}]_{\mathrm{i}} = [\mathrm{oxo}^{\bullet}] + [\mathrm{oxo\text{-}H}] \tag{S3}$$

$$[\mathrm{TEMPO\text{-}H}]_{\mathrm{i}} = [\mathrm{TEMPO\text{-}H}] + [\mathrm{TEMPO}^{\bullet}] \tag{S4}$$

$$[\mathrm{oxo\text{-}H}] = [\mathrm{TEMPO}^{\bullet}] \tag{S5}$$

The system of equations above were solved for [oxo$^{\bullet}$] and [TEMPO$^{\bullet}$], resulting in equations S6 and S7.

$$[\mathrm{oxo}^{\bullet}] = \frac{(\mathrm{Abs}^{\lambda}/l) - \varepsilon^{\lambda}_{\mathrm{TEMPO}\bullet}[\mathrm{oxo}\bullet]_{\mathrm{i}})}{\varepsilon^{\lambda}_{\mathrm{oxo}\bullet} - \varepsilon^{\lambda}_{\mathrm{TEMPO}\bullet}} \tag{S6}$$

$$[\mathrm{TEMPO}^{\bullet}] = \frac{(\mathrm{Abs}^{\lambda}/l) - \varepsilon^{\lambda}_{\mathrm{oxo}\bullet}[\mathrm{oxo}^{\bullet}]}{\varepsilon^{\lambda}_{\mathrm{TEMPO}\bullet}} \tag{S7}$$

For each sample A-G, the concentrations of all species at equilibrium were calculated from the absorbance at each integer wavelength, $\varepsilon^{\lambda}_{\mathrm{TEMPO}\bullet}$ and $\varepsilon^{\lambda}_{\mathrm{oxo}\bullet}$. A range of 450-550 nm was chosen due to the relatively large difference in ε between the species within these values. Representative data from sample B is provided in Table S2. At each wavelength (and for each sample) K_{eq} was determined using the calculated concentrations of the species at equilibrium, yielding an average $K_{\mathrm{eq}} = 3.9 \pm 2.0$. This corresponds to $\Delta G^{\circ} = -0.8 \pm 0.4$. Utilizing the known BDFE$_{\mathrm{hex}}$ of TEMPO-H (63.4 kcal mol^{-1}), the BDFE$_{\mathrm{hex}}$ of oxo-H was calculated to be 64.2 ± 0.4 kcal mol^{-1} (eq S1).

Table S2. UV–Vis spectroscopy data and calculated concentrations of reaction species from wavelengths 550-450 nm.

					Sample B, calculated values				
Wavelength (nm)	$\varepsilon_{\text{oxo}\bullet}$	$\varepsilon_{\text{TEMPO}\bullet}$	**Sample B, raw Abs data**	**Sample B, corrected Abs data**	**[oxo$^{\bullet}$]**	**[TEMPO$^{\bullet}$]**	**[oxo-H]**	**[TEMPO-H]**	K_{eq}
550	1.83	4.52	0.0765	0.0809	0.0167	0.0111	0.0111	0.00279	2.66
545	2.06	5.02	0.0858	0.0901	0.0168	0.0110	0.0110	0.00288	2.52
540	2.28	5.47	0.0945	0.0992	0.0167	0.0112	0.0112	0.00273	2.75
535	2.58	6.01	0.105	0.109	0.0170	0.0109	0.0109	0.00304	2.29
530	2.82	6.55	0.115	0.119	0.0169	0.0110	0.0110	0.00294	2.44
525	3.03	7.05	0.126	0.130	0.0164	0.0114	0.0114	0.00249	3.19
520	3.38	7.59	0.135	0.140	0.0170	0.0108	0.0108	0.00308	2.24
515	3.69	8.09	0.147	0.151	0.0168	0.0111	0.0111	0.00287	2.53
510	3.98	8.56	0.156	0.160	0.0170	0.0108	0.0108	0.00309	2.23
505	4.30	8.97	0.166	0.170	0.0171	0.0108	0.0108	0.00316	2.15
500	4.57	9.39	0.174	0.179	0.0170	0.0108	0.0108	0.00308	2.24
495	4.83	9.71	0.183	0.187	0.0171	0.0107	0.0107	0.00321	2.08
490	5.10	9.99	0.191	0.195	0.0170	0.0109	0.0109	0.00304	2.30
485	5.32	10.2	0.197	0.202	0.0169	0.0109	0.0109	0.00298	2.38
480	5.52	10.3	0.202	0.206	0.0168	0.0110	0.0110	0.00290	2.49
475	5.66	10.3	0.206	0.210	0.0165	0.0113	0.0113	0.00261	2.97
470	5.77	10.3	0.207	0.211	0.0167	0.0112	0.0112	0.00275	2.73
465	5.83	10.1	0.206	0.211	0.0166	0.0113	0.0113	0.00266	2.87
460	5.86	9.91	0.205	0.209	0.0164	0.0114	0.0114	0.00248	3.21
455	5.76	9.57	0.203	0.206	0.0159	0.0120	0.0120	0.00194	4.65
450	5.71	9.19	0.197	0.201	0.0157	0.0122	0.0122	0.00173	5.48

5 References

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