

Electrochemical Characterization and Thermodynamic Analysis of TEMPO Derivatives in Ionic Liquids

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Table S1: Proton transfer enthalpy and GFE of TEMPO derivatives with IL cations in kJ mol^{-1} .

Nitroxide	IL cation	IL anion	Enthalpy	GFE
4-cyano-TEMPO	C_1mim^+	$\text{N}(\text{CN})_2^-$	-73.1	-79.3
4-cyano-TEMPO	C_1mim^+	Mes^-	2.4	-4.0
4-cyano-TEMPO	C_1mim^+	NTf_2^-	-54.7	-52.1
4-cyano-TEMPO	C_1mim^+	BF_4^-	1.5	1.5
4-cyano-TEMPO	C_1mim^+	OTf^-	-30.1	-32.8
4-cyano-TEMPO	$\text{P}_{1,1,1,1}^+$	$\text{N}(\text{CN})_2^-$	-6.1	-6.9
4-cyano-TEMPO	$\text{P}_{1,1,1,1}^+$	Mes^-	10.9	9.9
4-cyano-TEMPO	$\text{P}_{1,1,1,1}^+$	NTf_2^-	23.5	26.0
4-cyano-TEMPO	$\text{P}_{1,1,1,1}^+$	BF_4^-	58.9	52.2
4-cyano-TEMPO	$\text{P}_{1,1,1,1}^+$	OTf^-	10.1	13.9
4-cyano-TEMPO	C_1mpyr^+	$\text{N}(\text{CN})_2^-$	23.6	23.3
4-cyano-TEMPO	C_1mpyr^+	Mes^-	123.1	121.9
4-cyano-TEMPO	C_1mpyr^+	NTf_2^-	94.5	82.0
4-cyano-TEMPO	C_1mpyr^+	BF_4^-	140.5	138.2
4-cyano-TEMPO	C_1mpyr^+	OTf^-	126.4	135.0
4-oxo-TEMPO	C_1mim^+	$\text{N}(\text{CN})_2^-$	-71.0	-78.6
4-oxo-TEMPO	C_1mim^+	Mes^-	5.6	-2.5
4-oxo-TEMPO	C_1mim^+	NTf_2^-	-124.6	-122.1
4-oxo-TEMPO	C_1mim^+	BF_4^-	0.7	-6.3
4-oxo-TEMPO	C_1mim^+	OTf^-	-74.2	-69.2
4-oxo-TEMPO	$\text{P}_{1,1,1,1}^+$	$\text{N}(\text{CN})_2^-$	-6.4	-5.4
4-oxo-TEMPO	$\text{P}_{1,1,1,1}^+$	Mes^-	9.0	11.3
4-oxo-TEMPO	$\text{P}_{1,1,1,1}^+$	NTf_2^-	18.2	13.8
4-oxo-TEMPO	$\text{P}_{1,1,1,1}^+$	BF_4^-	52.6	50.5
4-oxo-TEMPO	$\text{P}_{1,1,1,1}^+$	OTf^-	1.9	2.0
4-oxo-TEMPO	C_1mpyr^+	$\text{N}(\text{CN})_2^-$	116.9	105.7
4-oxo-TEMPO	C_1mpyr^+	Mes^-	119.2	114.6
4-oxo-TEMPO	C_1mpyr^+	NTf_2^-	97.0	97.0
4-oxo-TEMPO	C_1mpyr^+	BF_4^-	141.0	136.8
4-oxo-TEMPO	C_1mpyr^+	OTf^-	153.1	150.3
TEMPOL	C_1mim^+	$\text{N}(\text{CN})_2^-$	-70.7	-73.4
TEMPOL	C_1mim^+	Mes^-	7.1	6.0
TEMPOL	C_1mim^+	NTf_2^-	-127.4	-131.3
TEMPOL	C_1mim^+	BF_4^-	-23.3	-25.2
TEMPOL	C_1mim^+	OTf^-	-34.9	-39.9
TEMPOL	$\text{P}_{1,1,1,1}^+$	$\text{N}(\text{CN})_2^-$	-9.3	-12.0
TEMPOL	$\text{P}_{1,1,1,1}^+$	Mes^-	13.9	14.0

TEMPOL	$P_{1,1,1,1}^+$	NTf_2^-	5.9	10.8
TEMPOL	$P_{1,1,1,1}^+$	BF_4^-	58.1	56.3
TEMPOL	$P_{1,1,1,1}^+$	OTf^-	13.8	11.3
TEMPOL	C_1mpyr^+	$N(CN)_2^-$	21.2	22.6
TEMPOL	C_1mpyr^+	Mes^-	119.2	123.6
TEMPOL	C_1mpyr^+	NTf_2^-	43.8	43.0
TEMPOL	C_1mpyr^+	BF_4^-	135.2	137.3
TEMPOL	C_1mpyr^+	OTf^-	119.8	128.0

Table S2: Aminoxy and TEMPOH anion interaction energy with an IL IP in kJ mol⁻¹.

Nitroxide	Nitroxide	IL cation	IL anion	Electrostatic interaction	Dispersion interaction	Total interaction
4-cyano-TEMPO	Aminoxy	C ₁ mim ⁺	N(CN) ₂ ⁻	-89.3	-60.1	-149.3
4-cyano-TEMPO	Aminoxy	C ₁ mim ⁺	Mes ⁻	-93.1	-62.3	-155.4
4-cyano-TEMPO	Aminoxy	C ₁ mim ⁺	NTf ₂ ⁻	-107.4	-55.8	-163.1
4-cyano-TEMPO	Aminoxy	C ₁ mim ⁺	BF ₄ ⁻	-110.6	-48.0	-158.6
4-cyano-TEMPO	Aminoxy	C ₁ mim ⁺	OTf	-100.8	-62.2	-163.0
4-cyano-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	N(CN) ₂ ⁻	-135.8	-65.5	-201.3
4-cyano-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	Mes ⁻	-95.1	-64.8	-159.9
4-cyano-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	NTf ₂ ⁻	-138.1	-60.7	-198.8
4-cyano-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	BF ₄ ⁻	-115.9	-61.6	-177.4
4-cyano-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	OTf	-116.9	-66.5	-183.3
4-cyano-TEMPO	Aminoxy	C ₁ mpyr ⁺	N(CN) ₂ ⁻	-101.9	-71.3	-173.2
4-cyano-TEMPO	Aminoxy	C ₁ mpyr ⁺	Mes ⁻	-98.1	-50.7	-148.7
4-cyano-TEMPO	Aminoxy	C ₁ mpyr ⁺	NTf ₂ ⁻	-120.4	-68.0	-188.4
4-cyano-TEMPO	Aminoxy	C ₁ mpyr ⁺	BF ₄ ⁻	-115.3	-42.9	-158.3
4-cyano-TEMPO	Aminoxy	C ₁ mpyr ⁺	OTf	-131.9	-38.9	-170.8
4-oxo-TEMPO	Aminoxy	C ₁ mim ⁺	N(CN) ₂ ⁻	-94.9	-59.9	-154.8
4-oxo-TEMPO	Aminoxy	C ₁ mim ⁺	Mes ⁻	-88.7	-63.4	-152.2
4-oxo-TEMPO	Aminoxy	C ₁ mim ⁺	NTf ₂ ⁻	-93.4	-50.8	-144.2
4-oxo-TEMPO	Aminoxy	C ₁ mim ⁺	BF ₄ ⁻	-109.3	-53.3	-162.6
4-oxo-TEMPO	Aminoxy	C ₁ mim ⁺	OTf	-91.8	-67.7	-159.6
4-oxo-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	N(CN) ₂ ⁻	-136.9	-67.0	-203.9
4-oxo-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	Mes ⁻	-101.3	-63.4	-164.7
4-oxo-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	NTf ₂ ⁻	-142.0	-60.8	-202.8
4-oxo-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	BF ₄ ⁻	-120.8	-61.1	-181.9
4-oxo-TEMPO	Aminoxy	P _{1,1,1,1} ⁺	OTf	-118.8	-67.6	-186.4
4-oxo-TEMPO	Aminoxy	C ₁ mpyr ⁺	N(CN) ₂ ⁻	-110.0	-70.5	-180.4
4-oxo-TEMPO	Aminoxy	C ₁ mpyr ⁺	Mes ⁻	-103.8	-55.0	-158.9
4-oxo-TEMPO	Aminoxy	C ₁ mpyr ⁺	NTf ₂ ⁻	-127.0	-66.9	-193.9
4-oxo-TEMPO	Aminoxy	C ₁ mpyr ⁺	BF ₄ ⁻	-117.3	-43.0	-160.3
4-oxo-TEMPO	Aminoxy	C ₁ mpyr ⁺	OTf	-132.1	-40.2	-172.2
TEMPOL	Aminoxy	C ₁ mim ⁺	N(CN) ₂ ⁻	-107.1	-61.7	-168.8
TEMPOL	Aminoxy	C ₁ mim ⁺	Mes ⁻	-97.8	-53.1	-150.9
TEMPOL	Aminoxy	C ₁ mim ⁺	NTf ₂ ⁻	-98.5	-50.5	-149.0
TEMPOL	Aminoxy	C ₁ mim ⁺	BF ₄ ⁻	-119.7	-48.1	-167.7
TEMPOL	Aminoxy	C ₁ mim ⁺	OTf	-118.7	-59.3	-178.0
TEMPOL	Aminoxy	P _{1,1,1,1} ⁺	N(CN) ₂ ⁻	-123.9	-71.9	-195.8
TEMPOL	Aminoxy	P _{1,1,1,1} ⁺	Mes ⁻	-103.6	-63.6	-167.2
TEMPOL	Aminoxy	P _{1,1,1,1} ⁺	NTf ₂ ⁻	-153.3	-41.6	-194.9
TEMPOL	Aminoxy	P _{1,1,1,1} ⁺	BF ₄ ⁻	-127.8	-60.8	-188.6
TEMPOL	Aminoxy	P _{1,1,1,1} ⁺	OTf	-133.1	-64.3	-197.4
TEMPOL	Aminoxy	C ₁ mpyr ⁺	N(CN) ₂ ⁻	-108.6	-69.6	-178.2
TEMPOL	Aminoxy	C ₁ mpyr ⁺	Mes ⁻	-107.7	-46.7	-154.4

TEMPOL	Aminoxy	C ₁ mpyr ⁺	NTf ₂ ⁻	-143.0	-59.1	-202.1
TEMPOL	Aminoxy	C ₁ mpyr ⁺	BF ₄ ⁻	-123.8	-42.1	-165.9
TEMPOL	Aminoxy	C ₁ mpyr ⁺	OTf	-140.6	-38.5	-179.1
4-cyano-TEMPO	TEMPOH	C ₁ mim ⁺	N(CN) ₂ ⁻	-46.6	-56.2	-102.8
4-cyano-TEMPO	TEMPOH	C ₁ mim ⁺	Mes ⁻	-21.8	-57.7	-79.4
4-cyano-TEMPO	TEMPOH	C ₁ mim ⁺	NTf ₂ ⁻	-33.6	-59.4	-93.0
4-cyano-TEMPO	TEMPOH	C ₁ mim ⁺	BF ₄ ⁻	-61.9	-45.2	-107.1
4-cyano-TEMPO	TEMPOH	C ₁ mim ⁺	OTf	-34.0	-68.6	-102.7
4-cyano-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	N(CN) ₂ ⁻	-47.1	-40.6	-87.7
4-cyano-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	Mes ⁻	-66.3	-49.5	-115.9
4-cyano-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	NTf ₂ ⁻	-37.6	-57.7	-95.4
4-cyano-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	BF ₄ ⁻	13.0	-43.9	-30.9
4-cyano-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	OTf	-43.3	-56.7	-100.0
4-cyano-TEMPO	TEMPOH	C ₁ mpyr ⁺	N(CN) ₂ ⁻	-90.9	-63.9	-154.8
4-cyano-TEMPO	TEMPOH	C ₁ mpyr ⁺	Mes ⁻	12.2	-54.7	-42.5
4-cyano-TEMPO	TEMPOH	C ₁ mpyr ⁺	NTf ₂ ⁻	5.4	-50.9	-45.5
4-cyano-TEMPO	TEMPOH	C ₁ mpyr ⁺	BF ₄ ⁻	-0.3	-35.3	-35.6
4-cyano-TEMPO	TEMPOH	C ₁ mpyr ⁺	OTf	-5.1	-52.6	-57.7
4-oxo-TEMPO	TEMPOH	C ₁ mim ⁺	N(CN) ₂ ⁻	-46.9	-53.9	-100.9
4-oxo-TEMPO	TEMPOH	C ₁ mim ⁺	Mes ⁻	-27.9	-51.8	-79.6
4-oxo-TEMPO	TEMPOH	C ₁ mim ⁺	NTf ₂ ⁻	-35.6	-57.6	-93.2
4-oxo-TEMPO	TEMPOH	C ₁ mim ⁺	BF ₄ ⁻	-61.1	-43.7	-104.8
4-oxo-TEMPO	TEMPOH	C ₁ mim ⁺	OTf	-39.8	-66.1	-105.9
4-oxo-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	N(CN) ₂ ⁻	-40.9	-47.4	-88.2
4-oxo-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	Mes ⁻	-67.7	-49.0	-116.7
4-oxo-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	NTf ₂ ⁻	-39.6	-56.3	-96.0
4-oxo-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	BF ₄ ⁻	14.6	-46.4	-31.8
4-oxo-TEMPO	TEMPOH	P _{1,1,1,1} ⁺	OTf	-60.4	-49.1	-109.5
4-oxo-TEMPO	TEMPOH	C ₁ mpyr ⁺	N(CN) ₂ ⁻	-16.0	-30.7	-46.8
4-oxo-TEMPO	TEMPOH	C ₁ mpyr ⁺	Mes ⁻	2.1	-25.2	-23.1
4-oxo-TEMPO	TEMPOH	C ₁ mpyr ⁺	NTf ₂ ⁻	-29.3	-35.0	-64.3
4-oxo-TEMPO	TEMPOH	C ₁ mpyr ⁺	BF ₄ ⁻	6.6	-35.7	-29.0
4-oxo-TEMPO	TEMPOH	C ₁ mpyr ⁺	OTf	9.5	-36.9	-27.4
TEMPOL	TEMPOH	C ₁ mim ⁺	N(CN) ₂ ⁻	-36.1	-55.8	-91.9
TEMPOL	TEMPOH	C ₁ mim ⁺	Mes ⁻	1.5	-58.9	-57.4
TEMPOL	TEMPOH	C ₁ mim ⁺	NTf ₂ ⁻	-21.1	-58.7	-79.9
TEMPOL	TEMPOH	C ₁ mim ⁺	BF ₄ ⁻	-15.3	-64.8	-80.1
TEMPOL	TEMPOH	C ₁ mim ⁺	OTf	-16.4	-66.5	-83.0
TEMPOL	TEMPOH	P _{1,1,1,1} ⁺	N(CN) ₂ ⁻	-9.6	-68.0	-77.6
TEMPOL	TEMPOH	P _{1,1,1,1} ⁺	Mes ⁻	-43.7	-48.5	-92.2
TEMPOL	TEMPOH	P _{1,1,1,1} ⁺	NTf ₂ ⁻	16.5	-30.6	-14.1
TEMPOL	TEMPOH	P _{1,1,1,1} ⁺	BF ₄ ⁻	31.8	-47.8	-16.0
TEMPOL	TEMPOH	P _{1,1,1,1} ⁺	OTf	-34.5	-51.8	-86.3
TEMPOL	TEMPOH	C ₁ mpyr ⁺	N(CN) ₂ ⁻	-61.5	-64.1	-125.5
TEMPOL	TEMPOH	C ₁ mpyr ⁺	Mes ⁻	23.0	-52.2	-29.2
TEMPOL	TEMPOH	C ₁ mpyr ⁺	NTf ₂ ⁻	-71.9	-66.5	-138.4

TEMPOL	TEMPOH	C ₁ mpyr ⁺	BF ₄ ⁻	11.7	-36.7	-25.0
TEMPOL	TEMPOH	C ₁ mpyr ⁺	OTf	27.5	-39.4	-11.9

Table S3: Proton transfer enthalpy and GFEs of nitroxides by water surrounded by a single [C₁mim][BF₄] IP in kJ mol⁻¹.

Radical	Enthalpy	GFE
4-cyano-TEMPO	0.0	-0.9
4-oxo-TEMPO	-7.8	-12.6
TEMPO	17.4	15.1
TEMPOL	7.4	3.4

Table S4: Nitroxide aminoxy anion self-proton transfer enthalpy and GFE with nitroxide aminoxy anions and radicals with SMD ethanol implicit solvation and comparison of CCSD(T)/CBS with augmented and non-augmented basis sets in kJ mol⁻¹.

Radical	Basis Set	Reactant	Enthalpy	GFE
4-cyano-TEMPO	Augmented	Anion	56.8	59.3
4-cyano-TEMPO	Augmented	Radical	97.0	103.7
4-oxo-TEMPO	Augmented	Anion	-48.3	-47.6
4-oxo-TEMPO	Augmented	Radical	-56.3	-60.5
TEMPO	Augmented	Anion	107.6	103.2
TEMPO	Augmented	Radical	130.0	134.9
TEMPOL	Augmented	Anion	-19.3	-19.4
TEMPOL	Augmented	Radical	-12.2	-12.8
4-cyano-TEMPO	Non-Augmented	Anion	58.8	61.8
4-cyano-TEMPO	Non-Augmented	Radical	100.4	107.1
4-oxo-TEMPO	Non-Augmented	Anion	-47.9	-47.2
4-oxo-TEMPO	Non-Augmented	Radical	-58.1	-62.6
TEMPO	Non-Augmented	Anion	112.7	108.3
TEMPO	Non-Augmented	Radical	132.8	138.0
TEMPOL	Non-Augmented	Anion	-20.3	-20.4
TEMPOL	Non-Augmented	Radical	-13.2	-13.9

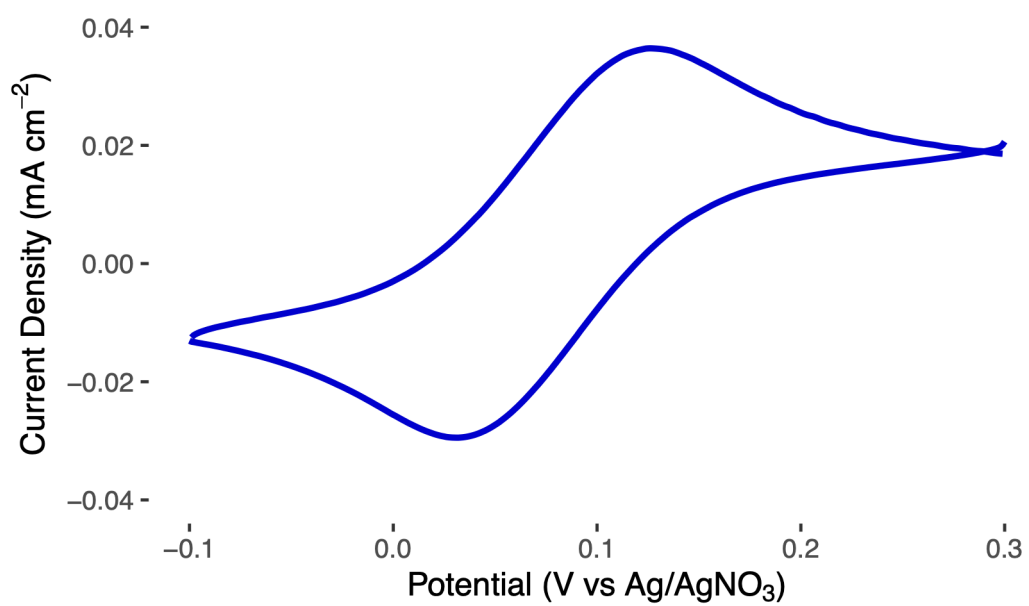


Figure S1: Sample CV of ferrocene in [C₄mpyr][OTf] against an Ag/AgNO₃ reference, taken from the 5th scan.