Electronic Supplementary Information for Dalton Transactions

Ion pairing in tetraphenylporphyrin oxidation: a semiquantitative study

Haoran Sun, Justin C. Biffinger and Stephen G. DiMagno*

Department of Chemistry and Center for Materials Research and Analysis, University of Nebraska-Lincoln, Lincoln, Nebraska, USA. Fax: 402 472-9402; Tel: 402 472-9895; E-mail: sdimagno1@unl.edu

1. Digital simulation parameters for measuring ion pairing equilibrium constants.
2. Z-matrix file of optimized $TPPH_2^{2+}$ dication structure
3. Cyclic voltammogram background of 0.1 M TBATFPB DFB solution.

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1. Digital simulation parameters for measuring ion pairing equilibrium constants.
Each of the ion pairing equilibrium constants, K_1, K_2 and K_3 was measured by cyclic voltammetry and digital simulation for cyclic voltammetry separately. At high concentration (0.1 M) of TBAX (X=PF_6^-, ClO_4^-, NTf_2^-, BF_4^-, and OTf^-), K_1 was measured by comparing the first oxidation potential to that in TBATFPB solution with identical concentration of free TBA cation (in order to keep the first reduction potential constant and to use it as an internal potential standard). At constant free TBA cation concentration, K_2 and K_3 were measured by cyclic voltammetric titration and digital simulation with different TBAX(X=PF_6^-, ClO_4^-, NTf_2^-, BF_4^-, and OTf^-).

a) Digital simulation for K_1

source program: DigiSim for Windows 95
program version: 3.05
file type: CV

charge transfer reactions:
reaction[1]: a + e = b

homogeneous chemical reactions:
reaction[1]: a + c = d
reaction[2]: f + c = g

experimental parameters:
Estart (V): 1.5
Eswitch (V): 2.5
Eend (V): 1.5
v (V/s): 0.1
temperature (K): 298.2
Ru (Ohms): 1000
Cdl (F): 2E-006
cycles: 1
electrode geometry: planar
area (cm2): 0.0314
diffusion: semi-infinite
pre-equilibrium: enabled for all reactions

charge transfer parameters:
E0[1] (V): 2.278
alpha[1]: 0.5
ks[1] (cm/s): 10

chemical reaction parameters:
Keq[1]: 520 (variable)
kf[1]: 1E+012

kb[1]: 1.9231E+009
Keq[2]: 1200
kf[2]: 1E+012
kb[2]: 8.3333E+008

species parameters:
Canal[a] (M/l): 0
Cinit[a] (M/l): 8.5246E-017
D[a] (cm2/s): 5E-006
Canal[b] (M/l): 0.0012
Cinit[b] (M/l): 0.0012
D[b] (cm2/s): 5E-006
Canal[c] (M/l): 0
Cinit[c] (M/l): 0.0087215
D[c] (cm2/s): 1E-005
Canal[d] (M/l): 0
Cinit[d] (M/l): 3.8656E-016
D[d] (cm2/s): 5E-006
Canal[f] (M/l): 0
Cinit[f] (M/l): 0.0087215
D[f] (cm2/s): 1E-005
Canal[g] (M/l): 0.1
Cinit[g] (M/l): 0.091278
D[g] (cm2/s): 1E-005

model parameters:
expanding space factor: 0.1
potential step (V): 0.001
iterations: 1
noise_level (A): 0
D/k: 50
xmax/sqrt(Dt): 6
r0 minimum: 20

simulation statistics:
CPU-time: 3.425
maximum number of boxes: 176
model diffusion coefficient: 1.0014E+012
total number of corrections: 0
number of potential steps with corrections: 0
Imin: -7.2176E-006
Imax: 5.2728E-006
Cmax: 0.091278

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b) Digital simulation for K_2

source program: DigiSim for Windows 95
program version: 3.05
file type: CV

charge transfer reactions:
reaction[1]: a + e = b
reaction[2]: b + e = c

homogeneous chemical reactions:
reaction[1]: d + f = g
reaction[2]: d + h = i
reaction[3]: a + h = j
reaction[4]: b + h = k

experimental parameters:
Estart (V): -0.2
Eswitch (V): 1.5
Eend (V): -0.2
v (V/s): 0.1
temperature (K): 298.2
Ru (Ohms): 1000
Cdl (F): 2E-006
cycles: 1
electrode geometry: planar
area (cm2): 0.0314
diffusion: semi-infinite
pre-equilibrium: enabled for all reactions

charge transfer parameters:
E0[1] (V): 1.377
alpha[1]: 0.5
ks[1] (cm/s): 10
E0[2] (V): 0.777
alpha[2]: 0.5
ks[2] (cm/s): 10

chemical reaction parameters:
Keq[1]: 65
kf[1]: 1E+012
kb[1]: 1.5385E+010
Keq[2]: 1200
kf[2]: 1E+012
kb[2]: 8.3333E+008

Keq[3]: 1.9E+006 (variable)
kf[3]: 1E+012
kb[3]: 5.2632E+005
Keq[4]: 520
kf[4]: 1E+012
kb[4]: 1.9231E+009

species parameters:
Canal[a] (M/l): 0
Cinit[a] (M/l): 8.2336E-047
D[a] (cm2/s): 5E-006
Canal[b] (M/l): 0
Cinit[b] (M/l): 3.694E-020
D[b] (cm2/s): 5E-006
Canal[c] (M/l): 0.0012
Cinit[c] (M/l): 0.0012
D[c] (cm2/s): 5E-006
Canal[d] (M/l): 0
Cinit[d] (M/l): 0.032065
D[d] (cm2/s): 1E-005
Canal[f] (M/l): 0
Cinit[f] (M/l): 0.032034
D[f] (cm2/s): 1E-005
Canal[g] (M/l): 0.0988
Cinit[g] (M/l): 0.066766
D[g] (cm2/s): 1E-005
Canal[h] (M/l): 0
Cinit[h] (M/l): 3.0397E-005
D[h] (cm2/s): 1E-005
Canal[i] (M/l): 0.0012
Cinit[i] (M/l): 0.0011696
D[i] (cm2/s): 1E-005
Canal[j] (M/l): 0
Cinit[j] (M/l): 4.755E-045
D[j] (cm2/s): 5E-006
Canal[k] (M/l): 0
Cinit[k] (M/l): 5.839E-022
D[k] (cm2/s): 5E-006

model parameters:
expanding space factor: 0.1
potential step (V): 0.001
iterations: 1
noise_level (A): 0
D/k: 50
xmax/sqrt(Dt): 6

r0 minimum: 20

simulation statistics:
CPU-time: 19.228
maximum number of boxes: 182
model diffusion coefficient: 2.0091E+012
total number of corrections: 0
number of potential steps with corrections: 0
Imin: -8.5306E-006
Imax: 6.5465E-006
Cmax: 0.067081

c) Digital simulation for K_3

source program: DigiSim for Windows 95
program version: 3.05
file type: CV

charge transfer reactions:
reaction[1]: a + e = b
reaction[2]: b + e = c

homogeneous chemical reactions:
reaction[1]: d + f = g
reaction[2]: d + h = i
reaction[3]: a + h = j
reaction[4]: j + h = l
reaction[5]: b + h = k

experimental parameters:
Estart (V): -0.2
Eswitch (V): 1.5
Eend (V): -0.2
v (V/s): 0.1
temperature (K): 298.2
Ru (Ohms): 1000
Cdl (F): 2E-006
cycles: 1
electrode geometry: planar
area (cm2): 0.0314
diffusion: semi-infinite
pre-equilibrium: enabled for all reactions

charge transfer parameters:
E0[1] (V): 1.377
alpha[1]: 0.5
ks[1] (cm/s): 10
E0[2] (V): 0.777
alpha[2]: 0.5
ks[2] (cm/s): 10

chemical reaction parameters:
Keq[1]: 65
kf[1]: 1E+012
kb[1]: 1.5385E+010
Keq[2]: 1200
kf[2]: 1E+012

kb[2]: 8.3333E+008
Keq[3]: 1.9E+006
kf[3]: 1E+012
kb[3]: 5.2632E+005
Keq[4]: 6700 (variable)
kf[4]: 1E+012
kb[4]: 1.4925E+008
Keq[5]: 520
kf[5]: 1E+012
kb[5]: 1.9231E+009

species parameters:
Canal[a] (M/l): 0
Cinit[a] (M/l): 8.2335E-047
D[a] (cm2/s): 5E-006
Canal[b] (M/l): 0
Cinit[b] (M/l): 3.694E-020
D[b] (cm2/s): 5E-006
Canal[c] (M/l): 0.0012
Cinit[c] (M/l): 0.0012
D[c] (cm2/s): 5E-006
Canal[d] (M/l): 0
Cinit[d] (M/l): 0.030279
D[d] (cm2/s): 1E-005
Canal[f] (M/l): 0
Cinit[f] (M/l): 0.029985
D[f] (cm2/s): 1E-005
Canal[g] (M/l): 0.089
Cinit[g] (M/l): 0.059015
D[g] (cm2/s): 1E-005
Canal[h] (M/l): 0
Cinit[h] (M/l): 0.00029463
D[h] (cm2/s): 1E-005
Canal[i] (M/l): 0.011
Cinit[i] (M/l): 0.010705
D[i] (cm2/s): 1E-005
Canal[j] (M/l): 0
Cinit[j] (M/l): 4.6075E-044
D[j] (cm2/s): 5E-006
Canal[l] (M/l): 0
Cinit[l] (M/l): 9.095E-044
D[l] (cm2/s): 5E-006
Canal[k] (M/l): 0
Cinit[k] (M/l): 5.6595E-021
D[k] (cm2/s): 5E-006

model parameters:
expanding space factor: 0.1
potential step (V): 0.005
iterations: 1
noise_level (A): 0
D/k: 50
xmax/sqrt(Dt): 6
r0 minimum: 20

simulation statistics:
CPU-time: 5.237
maximum number of boxes: 183
model diffusion coefficient: 1.2546E+013
total number of corrections: 90
number of potential steps with corrections: 3
Imin: -9.2998E-006
Imax: 6.7587E-006
Cmax: 0.05954

2. Z-matrix file of optimized $TPPH_2^{2+}$ dication structure

Calculated by DFT at B3LYP/6-311G* level

N
C,1,R2
C,1,R2,2,A3
C,2,R4,1,A4,3,D4,0
C,2,R5,1,A5,4,D5,0
C,3,R4,1,A4,2,-D4,0
C,3,R5,1,A5,6,-D5,0
C,7,R8,3,A8,1,D8,0
C,5,R8,2,A8,1,-D8,0
C,5,R10,2,A10,9,D10,0
C,7,R10,3,A10,8,-D10,0
H,4,R12,2,A12,1,D12,0
H,6,R12,3,A12,1,-D12,0
N,8,R14,7,A14,3,D14,0
N,9,R14,5,A14,2,-D14,0
C,8,R16,7,A16,14,D16,0
C,9,R16,5,A16,15,-D16,0
C,11,R18,7,A18,3,D18,0
C,11,R19,7,A19,18,D19,0
C,10,R18,5,A18,2,-D18,0
C,10,R19,5,A19,20,-D19,0
H,14,R22,8,A22,7,D22,0
H,15,R22,9,A22,5,-D22,0
C,14,R14,8,A24,22,D24,0
C,15,R14,9,A24,23,-D24,0
C,16,R26,8,A26,7,D26,0
C,17,R26,9,A26,5,-D26,0
C,18,R28,11,A28,7,D28,0
C,19,R29,11,A29,7,D29,0
C,20,R28,10,A28,5,-D28,0
C,21,R29,10,A29,5,-D29,0
H,16,R32,8,A32,26,D32,0
H,17,R32,9,A32,27,-D32,0
H,18,R34,11,A34,28,D34,0
H,19,R35,11,A35,29,D35,0
H,20,R34,10,A34,30,-D34,0
H,21,R35,10,A35,31,-D35,0
C,24,R8,14,A14,8,D38,0
C,25,R8,15,A14,9,-D38,0
C,30,R40,20,A40,10,D40,0
C,28,R40,18,A40,11,-D40,0

H,26,R32,16,A42,8,D42,0
H,27,R32,17,A42,9,-D42,0
H,28,R44,18,A44,41,D44,0
H,29,R45,19,A45,11,D45,0
H,30,R44,20,A44,40,-D44,0
H,31,R45,21,A45,10,-D45,0
C,39,R5,25,A8,15,D14,0
C,38,R5,24,A8,14,-D14,0
C,38,R10,24,A50,49,D50,0
C,39,R10,25,A50,48,-D50,0
H,40,R52,30,A52,20,D52,0
H,41,R52,28,A52,18,-D52,0
N,48,R2,39,A5,25,D8,0
C,48,R4,39,A55,54,D55,0
C,49,R4,38,A55,24,D56,0
C,50,R18,38,A18,24,D57,0
C,50,R19,38,A19,57,-D19,0
C,51,R18,39,A18,25,-D57,0
C,51,R19,39,A19,59,D19,0
C,57,R28,50,A28,38,-D28,0
C,58,R29,50,A29,38,-D29,0
C,59,R28,51,A28,39,D28,0
C,60,R29,51,A29,39,D29,0
H,55,R12,48,A12,39,D65,0
H,56,R12,49,A12,38,-D65,0
H,57,R34,50,A34,61,-D34,0
H,58,R35,50,A35,62,-D35,0
H,59,R34,51,A34,63,D34,0
H,60,R35,51,A35,64,D35,0
C,63,R40,59,A40,51,-D40,0
C,61,R40,57,A40,50,D40,0
H,61,R44,57,A44,72,-D44,0
H,62,R45,58,A45,50,-D45,0
H,63,R44,59,A44,71,D44,0
H,64,R45,60,A45,51,D45,0
H,71,R52,63,A52,59,-D52,0
H,72,R52,61,A52,57,D52,0

Variables:

R2=1.36435492
R4=1.45126812
R5=1.42084485
R8=1.4312643
R10=1.46252088
R12=1.07843433
R14=1.36994299
R16=1.41785631

R18=1.41416667
R19=1.41458246
R22=1.00988437
R26=1.38068494
R28=1.38589718
R29=1.3860933
R32=1.07761001
R34=1.08321514
R35=1.08345076
R40=1.39736403
R44=1.08394328
R45=1.08394677
R52=1.08428537
A3=104.97276713
A4=111.25606401
A5=124.12725346
A8=123.83476838
A10=119.02897011
A12=126.34696157
A14=125.70853545
A16=127.0996711
A18=120.51627403
A19=120.88167618
A22=124.80888358
A24=110.07493217
A26=107.75462249
A28=120.46314907
A29=120.48637394
A32=125.33553951
A34=119.62429279
A35=119.72164198
A40=120.13181587
A42=126.86606239
A44=119.81331426
A45=119.83690123
A50=117.13522142
A52=119.91666573
A55=124.58955565
D4=-4.09317089
D5=178.17878836
D8=-15.34199318
D10=-179.6178497
D12=-174.5525606
D14=-17.28101543
D16=-178.540081
D18=-45.60801749

D19=179.99161644
D22=9.73203351
D24=173.87975298
D26=177.31960915
D28=-179.0446094
D29=-178.83387727
D32=177.72738884
D34=176.32056643
D35=176.07337393
D38=176.38821351
D40=2.08602443
D42=177.6826566
D44=179.73508649
D45=177.54152323
D50=179.62453069
D52=178.90175737
D55=-177.9381535
D56=-166.71985331
D57=-134.03529079
D65=-7.27872838

3. Cyclic voltammogram background of 0.1 M TBATFPB DFB solution.

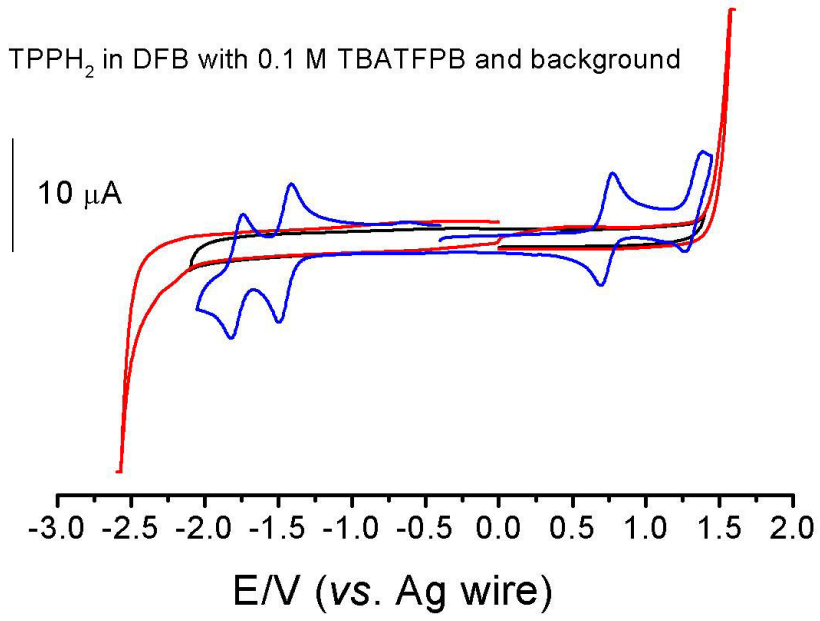

Figure S-1 Cyclic voltammograms of 0.1 M TBATFPB DFB solution (black and red lines) and $TPPH_2$ in 0.1 M TBATFPB DFB solution (blue line). Scan rate, 100 mV/s.