

## Sample 1

### Electrochemistry of Oxygen in Concentrated NaOH Solutions: Solubility, Diffusion Coefficients, and Superoxide Formation

Cunzhong Zhang<sup>‡</sup>, Fu-Ren F. Fan and Allen J. Bard\*

Center for Electrochemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712-0165

*J. Am. Chem. Soc.*, Article ASAP

Publication Date (Web): December 8, 2008

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#### Experimental Section

##### Chemicals

NaOH (ACS reagent grade) was dissolved in Milli-Q water to make a series of concentrations of NaOH aqueous solution, from 1 to 12 M. NaOH solutions, saturated with either highly pure Ar or O<sub>2</sub>, were employed as the blank or working solution, respectively.

##### Techniques and Apparatus

All electrochemical measurements were carried out on a CHI model 660 electrochemical workstation or a CHI 900 SECM system (CH Instruments, Austin, TX) at 296 ± 0.5 K. A large-area Ti screw was used as the counter electrode. A HgO/Hg (14 M NaOH) electrode, placed within a Luggin capillary, was used as the reference electrode (0.006 V vs SHE). A Pt disk UME was constructed by sealing Pt wire in borosilicate glass, with a Pt disk diameter of 25 μm and RG (the ratio of total radius of the tip to radius of the Pt disk) of 3.5, and was used as a working electrode or SECM tip. It is known that strongly alkaline solutions can etch glass, and we were concerned that, upon exposure to our test solutions, the electrode would develop leaks around the metals. However, experiments with the NaOH solutions as well as characterization of the tips before and after extended exposure to concentrated NaOH solutions did not show any behavior that suggested the development of leaks, although there appeared to be considerable roughening of the electrode on continuous cycling in strongly alkaline solutions (Figure 1). A Pt disk electrode (diameter of 2.1 mm), sealed in soft glass, was used as the collector or substrate in SECM experiments and was employed as a working electrode for some electrochemical measurements. Prior to each experiment, the surfaces of Pt UMEs and Pt disk electrodes were polished with 0.3 μm alumina and then cycled in Ar-saturated NaOH solution at a scan rate of 50 mV/s between the onset potentials of hydrogen and oxygen evolution reactions until reproducible cyclic voltammograms were obtained. The final potential was stopped at the onset potential of hydrogen evolution.

## Sample 2

### Enantioselective Nitroaldol Reaction Catalyzed by Sterically Modified Salen–Chromium Complexes

Rafał Kowalczyk<sup>‡</sup>, Piotr Kwiatkowski<sup>‡</sup>, Jacek Skarżewski<sup>\*‡</sup> and Janusz Jurczak<sup>\*‡§</sup>

Department of Organic Chemistry, Faculty of Chemistry, Wrocław University of Technology, 50-370 Wrocław, Poland, Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland, and Department of Chemistry, University of Warsaw, 02-093 Warsaw, Poland

*J. Org. Chem.*, Article ASAP

Publication Date (Web): December 8, 2008

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#### Experimental Section

##### General Procedure for Catalyst Screening in the Nitroaldol Reaction of Benzaldehyde with Nitromethane (Table 1)

Salen–chromium(III) complex **1a–h** (0.01 mmol, 2 mol%) was placed in a 10 mL reaction vessel and dissolved in dichloromethane (0.5 mL). After the complex was cooled to –78 °C (acetone–dry ice bath), benzaldehyde (53 mg, 51 μL, 0.5 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) followed by nitromethane (2.0 mL) and solution of DIPEA (86 μL, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) were added at 5 min intervals. The resulting solution was stirred for 0.5 h at –78 °C, then put into the freezer (–20 °C) for 20 h, and finally diluted with *n*-hexane (5 mL). Purification by flash chromatography on silica gel (gradient *n*-hexane/AcOEt 9:1–7:3, v/v) afforded the desired nitro alcohol **5a**.

### (S)-1-Phenyl-2-nitroethanol (5a):(13)

77% yield;  $[\alpha]_D^{25} = +41.7$  (c 0.28, CH<sub>2</sub>Cl<sub>2</sub>), 93% ee by HPLC analysis (Chiracel OD-H column, 1.0 mL/min, *n*-hexane/*i*-PrOH 90:10,  $\lambda = 206$  nm), (*R*)-isomer  $t_R = 13.33$  min and (*S*)-isomer  $t_R = 16.19$  min; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.35–7.41 (m, 5H), 5.46 (dd,  $J = 9.6, 2.9$  Hz, 1H), 4.61 (dd,  $J = 13.4, 9.6$  Hz, 1H), 4.52 (dd,  $J = 13.4, 3.0$  Hz, 1H), 2.82 (bs, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  138.1, 129.0, 128.9, 125.9, 81.2, 71.0.

### General Procedure for the Optimized Nitroaldol Reaction Catalyzed by Complex 1h (Table 3)

Complex 1h (8.2 mg, 0.02 mmol, 2 mol %) was dissolved in dichloromethane (0.5 mL) in a 5 mL reaction vessel stoppered with a rubber septum. The resulted brown solution was cooled to  $-78$  °C, and a solution of the respective aldehyde (1.0 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added via syringe. After 5 min, nitromethane (100  $\mu$ L, 2.0 mmol, 2.0 equiv) followed by DIPEA (172  $\mu$ L, 1.0 mmol, 1.0 equiv) were infused. The reaction mixture was stirred 0.5 h at  $-78$  °C and then left at  $-20$  °C in the refrigerator for 20 h. Dilution by *n*-hexane and purification by flash chromatography on silica gel (gradient *n*-hexane/AcOEt 9:1–7:3, v/v) afforded the desired products 5a–m. Ee's were determined by HPLC on chiral columns (Chiralcel OD-H or Chiralpak AD-H).

### Catalyst 1h

Prepared according to the Jacobsen procedure. (1*R*,2*R*)-1h:  $[\alpha]_D = -1420.0$  (c 0.01 CHCl<sub>3</sub>); IR (KBr)  $\nu$  3429, 2961, 1622 ( $\nu_{C=N}$ ), 1533, 1437, 1258, 700, 546 cm<sup>-1</sup>; HRMS calcd for C<sub>50</sub>H<sub>64</sub>N<sub>2</sub>O<sub>2</sub>Cr (ESI [M – Cl]<sup>+</sup>) 776.4373, found 776.4392. Anal. Calcd for C<sub>50</sub>H<sub>64</sub>N<sub>2</sub>O<sub>2</sub>CrCl: C, 73.91; H, 7.94; N, 3.45; Cl, 4.36. Found: C, 73.76; H, 8.10; N, 3.17; Cl, 4.35.

### Precursors of Catalyst 1h

#### 4-*tert*-Butyl-2-(3-phenylpent-3-yl)phenol (2h)

To stirred solution of *p*-*tert*-butylphenol (6.0 g, 40.0 mmol) and 3-phenylpent-2-ene (9.76 g, 60 mmol, 1.5 equiv) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was added methanesulfonic or sulfuric acid (2 mL) dropwise at 0 °C. The resulting solution was stirred overnight at room temperature. Then water (30 mL) and CH<sub>2</sub>Cl<sub>2</sub> (30 mL) were added, and the organic phase was separated, washed with saturated NaHCO<sub>3</sub>, dried with MgSO<sub>4</sub>, and concentrated. The resulting crude reaction mixture was dissolved in a minimum volume of hot EtOH and crystallized giving the product with 52% yield as a colorless crystals: mp = 120–122 °C; IR (film)  $\nu$  3504, 2965, 2950, 2877, 1494, 1209, 824, 764, 704 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (d,  $J = 2.4$  Hz, 1H), 7.38–7.19 (m, 5H), 7.16 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.65 (d,  $J = 8.4$  Hz, 1H), 3.81 (bs, 1H), 2.30–1.95 (m, 4H), 1.35 (s, 9H), 0.60 (t,  $J = 7.3$  Hz, 6H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 146.4, 142.3, 132.1, 128.9, 127.4, 126.9, 125.2, 124.3, 117.0, 48.4, 34.3, 31.7, 27.4, 8.3; HRMS calcd for C<sub>21</sub>H<sub>28</sub>ONa (ESI, [M + Na]<sup>+</sup>) 319.2032, found 319.2040.

#### 5-*tert*-Butyl-2-hydroxy-3-(3-phenylpent-3-yl)benzaldehyde (3h)

Prepared according to the Casiraghi procedure: (11) yield 70%, light yellow crystals; mp = 96–97 °C, crystallized from MeOH; IR (KBr)  $\nu$  3059, 2961, 2875, 1644, 1611, 1446, 1259, 1210, 761, 698, 545 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.17 (d,  $J = 0.6$  Hz, 1H), 9.79 (s, 1H), 7.77 (d,  $J = 2.4$  Hz, 1H), 7.37 (d,  $J = 2.4$  Hz, 1H), 7.24–7.20 (m, 2H), 7.14–7.12 (m, 3H), 2.41 (dt,  $J = 7.3$  Hz, 2H), 2.04 (dt,  $J = 7.3$  Hz, 2H), 1.38 (s, 9H), 0.60 (t,  $J = 7.4$  Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  196.9, 158.4, 147.7, 141.1, 135.1, 133.9, 127.8, 127.4, 126.9, 125.1, 119.9, 48.7, 34.2, 31.3, 26.9, 8.5; HRMS calcd for C<sub>22</sub>H<sub>28</sub>O<sub>2</sub>Na (ESI [M + Na]<sup>+</sup>) 347.1982, found 347.1998.

#### (1*R*,2*R*)-*N,N'*-Bis[5-*tert*-butyl-3-(3-phenylpent-3-yl)salicylidene]-1,2-cyclohexanediamine (4h)

Prepared according to the Jacobsen procedure. (5) A round-bottom, 150 mL flask was charged with (1*R*,2*R*)-cyclohexanediamine L-tartrate salt (2.65 g, 10 mmol, 1.0 equiv), K<sub>2</sub>CO<sub>3</sub> (3.1 g, 22 mmol), and water (12 mL). The resulted mixture was stirred for 10 min followed by addition of ethanol (96%, 50 mL) and heated to 60–70 °C for 0.5 h. The temperature was maintained, and aldehyde 3h (6.82 g, 21 mmol) was added in one portion. The mixture was vigorously stirred and refluxed for 3 h. Ligand 4h oiled out from the reaction mixture. The mixture was concentrated to ca. 1/4 of its initial volume, dissolved in CH<sub>2</sub>Cl<sub>2</sub> (75 mL), and washed with water (2  $\times$  50 mL). The organic phase was dried and concentrated to give a yellow solid which was dissolved in 25 mL of hot ethanol. The resulting solution was cooled to ambient temperature, and 10 mL of 50% aqueous ethanol was added to produce yellow precipitate that was collected with 81% yield: yellow crystals; mp = 92–94 °C;  $[\alpha]_D = +325.6$  (c 0.53, CHCl<sub>3</sub>); IR (KBr)  $\nu$  2963, 2875, 1628 ( $\nu_{C=N}$ ), 1597, 1445, 1263, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  13.10 (s, 2H), 7.98 (s, 2H), 7.43 (d,  $J = 2.4$  Hz, 2H), 7.08–7.20 (m, 10H), 6.89 (d,  $J = 2.4$  Hz, 2H), 3.02–3.07 (m, 2H), 2.28–2.44 (m, 4H), 1.98–2.07 (m, 4H), 1.70–1.80 (m, 4H), 1.49–1.59 (m, 2H), 1.29–1.32 (m, 2H), 1.28 (s, 18H), 0.57 (t,  $J = 7.3$  Hz, 6H), 0.51 (t,  $J = 7.3$  Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  165.6, 157.5, 148.6, 139.2, 133.2, 129.2, 127.2, 127.0, 125.9, 124.7, 117.6, 72.3, 49.0, 34.0, 32.9, 31.4, 28.1, 27.2, 24.2; HRMS calcd for C<sub>50</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>Na (ESI [M + Na]<sup>+</sup>) 749.5022, found 749.5021. Anal. Calcd for C<sub>50</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>: C, 82.60; H, 9.15; N, 3.85. Found: C, 82.55; H, 9.23; N, 3.83.



## Sample 3

### Computers and Chemical Engineering

pp: 2877-2890

Vol: 32 Issue: 12, December 22, 2008

### **Three-dimensional numerical study of heat and mass transfer in fluidized beds with spray nozzle**

Chamakuri Nagaiah <sup>a</sup>  , Gerald Warnecke <sup>a</sup>, Stefan Heinrich <sup>b</sup>, Mirko Peglow <sup>c</sup>

<sup>a</sup> Institute for Analysis and Numerics, Otto-von-Guericke University, PSF 4120, D-39106 Magdeburg, Germany

<sup>b</sup> Institute of Process Equipment and Environmental Technology, Otto-von-Guericke University, PSF 4120, D-39106 Magdeburg, Germany

<sup>c</sup> Institute of Process Engineering, Otto-von-Guericke University, PSF 4120, D-39106 Magdeburg, Germany

#### 5. Simulation results

The three space dimensional transient numerical simulations of balance equations are presented in this section. The fluidized bed zone is represented by a cylinder in the numerical simulation. The initial mesh and successive uniform mesh refinements are done using the program package UG (Unstructured Grid), see [Bastian et al. \(1997\)](#). The hexahedron element, which has 8 nodes and 6 surfaces, is used in the mesh generation. The initial mesh (level 0), consists of 8 hexahedron elements, and the fine mesh (level 4) consists of 32,768 elements, that are obtained by using uniform mesh refinement, see [Fig. 2](#).

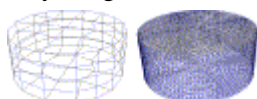


Fig. 2: Initial mesh and uniform refinement mesh at level 4.

The simulation results of the balance quantities air humidity, air temperature, degree of wetting, liquid film temperature, particle temperature and saturated air humidity are presented. In the numerical simulations, the sprayed liquid is considered as water. To compare our numerical results with experiments, we have considered 2 sets of experimental data for the numerical simulations. The first set of data is taken from the doctoral thesis of [Heinrich \(2001\)](#) and second set of data is taken from the doctoral thesis of [Henneberg \(2004\)](#).

#### 5.1. Experiment 1

The simulation parameters are shown in [Table 1](#) for the first test case. In this case one spray nozzle is considered in the simulation, which is fixed at  $(0.2, 0.2, 0.2)$  on a cylindrical domain with spray angle  $\theta = 45^\circ$ . The model equations and our program allow the flexibility to arrange more than one nozzle positions arbitrarily. In the numerical simulation Eq. (13) is used to calculate the spatial profile of the spray nozzle. Here, the bed mass  $m_P = 20$  kg and mass flow of the nozzle  $\dot{m}_L = 13.79$  kg/h are considered. Initial and boundary values, which are used in simulations, are shown in [Table 1](#).

## Sample 4

### Polymer

Vol: 49 Issue: 23, October 30, 2008

pp: 4995-5001

### **Synthesis, characterization and optical properties of fluorinated poly(aryl ether)s containing phthalazinone moieties**

Yuan Song <sup>a</sup>, Jinyan Wang <sup>a</sup>, Guanghui Li <sup>a</sup>, Qingmin Sun <sup>a</sup>, Xigao Jian <sup>a,c</sup>  , Jie Teng <sup>b,c</sup>, Hongbo Zhang <sup>a</sup>

<sup>a</sup> Department of Polymer Science & Materials, Dalian University of Technology, Dalian 116012, PR China

<sup>b</sup> School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116023, PR China

<sup>c</sup> Photonics Research Center, Dalian University of Technology, Dalian 116023, PR China

#### 2.1. Materials

4-(4'-Hydroxyphenyl)phthalazin-1(2H)-one (DHPZ) was gifted by Dalian Polymer New Material Co. Ltd., PR China, and recrystallized in N,N -dimethylacetamide (DMAc), subsequently, it was dried in vacuum at 120 °C for 24 h before use. 4,4'-(Hexafluoroisopropylidene)diphenol (6F-BPA) and decafluorobiphenyl (DFBP) were purchased from Sigma-Aldrich and used without further purification. Analytical-grade anhydrous potassium fluoride (KF) and calcium hydride (CaH<sub>2</sub>) (Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China) were used as received. Analytical-grade N,N' -dimethylacetamide (DMAc) (Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China) was purified by reduced pressure distillation prior to use, subsequently, the middle fractions were collected and stored over molecular sieves (Type 4 Å). All the other chemicals were of analytical-grade and purchased from Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China. And they were used without further purification unless otherwise noted.

## 2.2. Measurements

<sup>1</sup>H NMR (400 MHz) and <sup>19</sup>F NMR (376 MHz) spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25 °C using CDCl<sub>3</sub> as a solvent and were listed in parts per million downfield from tetramethylsilane (TMS) and potassium fluoride (KF), respectively. Fourier transform infrared (FT-IR) spectra were recorded by reflection method with a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer. Gel permeation chromatography (GPC) analysis was carried out on a HP 1090 HPLC instrument equipped with 5 μm Phenogel columns (linear, 4 × 500 Å) arranged in series with THF as solvent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. The glass transition temperatures (T<sub>g</sub>s) were determined with a Mettler DSC822 differential scanning calorimetry (DSC) in flowing nitrogen at a heating rate of 10 °C min<sup>-1</sup> from 50 to 400 °C. Thermogravimetric analysis (TGA) of the polymers was performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20 °C min<sup>-1</sup> from 100 to 700 °C. Optical properties such as refractive index, optical loss and thermo-optic coefficient value ( $dn/dT$ ) were measured by using a Sairon SPA-4000 prism coupler with the tolerance of ±0.0002.

## 2.3. Polymer synthesis

A series of novel fluorinated poly(phthalazinone ether)s (FPPEs) were synthesized via a modified nucleophilic aromatic substitution (S<sub>N</sub>AR) polycondensation reaction as illustrated in [Scheme 1](#). A typical preparation of these polymers (FPPE-2) was illustrated as follows. Potassium fluoride (KF, 16 mmol) and calcium hydride (CaH<sub>2</sub>, 40 mmol) were added to a solution of 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA, 15 mmol), 4-(4'-hydroxyphenyl)phthalazin-1(2H)-one (DHPZ, 5 mmol) and decafluorobiphenyl (DFBP, 20 mmol) in 10 mL of anhydrous *N,N'*-dimethylacetamide (DMAc). Nitrogen was purged through the reaction mixture with stirring for 10 min, and then the mixture was slowly heated to 90 °C and kept at this temperature for 4 h. After cooling, the viscous solution was slowly poured into sufficient ethanol under vigorous stirring to precipitate the product. After filtered and dried, the polymer was purified by filtering its *N,N'*-dimethylacetamide (DMAc) solution through a thin layer of Celite545 (0.02–0.1 mm) before precipitating it into sufficient ethanol. The white powder was collected by filtration and then treated thoroughly with boiling pure water, followed by filtration, washing thoroughly with pure water and methanol, and then drying at 60 °C under vacuum for 24 h. The total yield of FPPE-2 was 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.06 (d, *J* = 8.5 Hz, 12H), 7.24 (d, *J* = 9.9 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 12H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.80–8.00 (3H, m), 8.63 (1H, m). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ: -64.07 (20F, s), -136.61 (2F, m), -137.44 (16F, m), -143.31 (2F, m), -152.42 (16F, m). IR (film, cm<sup>-1</sup>): 1696 (C=O), 1608, 1487 (aromatic ring), 1260, 1229 (aromatic ether bond).

The following polymers with different fluorine contents were prepared using the same procedure as outlined above and characterized as follows.

**FPPE-1** : 94% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.05 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ: -64.09 (3F, s), -137.45 (2F, m), -152.37 (2F, m). IR (film, cm<sup>-1</sup>): 1609, 1509, 1488 (aromatic ring, C=C), 1261, 1229 (C–O–C).

## 2.4. Film preparation and optical properties measurements

The substrates used in the experiments were highly polished Si/SiO<sub>2</sub> wafers. Organic residues on the silicon surfaces were removed by the successive ultrasonic cleaning with acetone, alcohol and ion free pure water. The polymers were dissolved in cyclohexanone at a concentration of 20 wt%. Then the solution was filtered through a 0.45 μm Teflon microfilter and spin-coated on a Si/SiO<sub>2</sub> substrate. The spin-coating speeds ranged from 1000 to 6000 rpm. And the spinning time was 30 seconds. In order to guarantee the quality of the spin-coated films, the whole spin-coating procedure was carried out in a 1000 class ultraclean room. The resulting films were dried at 60 °C (30 min) and 120 °C (4 h) to remove the residual solvent under vacuum. The refractive indices of the polymer films were measured by using a Sairon SPA-4000 prism coupler at the wavelengths of 1310 nm and 1550 nm with the tolerance of ±0.0002. The optical losses of the polymer films were measured on slab waveguide samples using the high-index liquid immersion technique on a Sairon SPA-4000 prism coupler, which gave a precise measurement down to 0.05 dB/cm [30,31] [30, 31]. In this technique, light was coupled to a slab waveguide by prism coupling. After propagating a certain distance, the light was out-coupled from the waveguide by immersing it into the liquid oil with an index of refraction slightly higher than that of the film (herein, the refractive index of the oil was 1.60.). And the propagation loss could be calculated with the out-coupled intensity of the guided light described as a function of the propagation distance.