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Electrochemical Reduction of Pyrrole in the Presence of Trinitrofluorenone: Isolation of a Meisenheimer Complex

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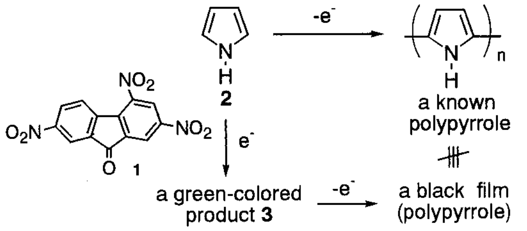
Polypyrrole is one of the most important conducting polymers,[1] and electrochemical polymerization is used for its film preparation.[2] On the other hand 2,4,7-trinitrofluoren-9-one (TNF) (**1**) is the best known electron-transporting material.[3] In a study on the electrochemical preparation of alternative films, we have found that pyrrole (**2**) is electrochemically reduced to a green-colored product **3** in the presence of **1** and polymerized into a novel film by the subsequent electro-oxidation. Spectroscopic investigation of **3** led to its characterization as a Meisenheimer complex of **1** and **2**. In this communication we present the first isolation of an electrochemically induced Meisenheimer complex including a nonbasic **2**, together with a mechanistic rationale for the formation of the complex.

A solution of a mixture of **1** (0.02 M) and **2** (0.02 M) in acetonitrile (CH_3CN) containing tetraethylammonium perchlorate ($Et_4N^+ClO_4^-$) (0.1 M) as a supporting electrolyte was subjected to electroreduction under ice-cooling at a constant potential of −1.0 V vs a saturated calomel electrode (SCE) in a two-compartment type cell equipped with a platinum gauze cathode (3.5 × 12.5 cm^2, 55 mesh) and a platinum plate anode (3.0 × 2.5 cm^2) under a flow of nitrogen (N_2). An electric current was passed for 27 h resulting in passage of 2 Faraday per mol of **1** for generation of a dianion $\mathbf{1}^{2-}$, during which time the color of the reaction mixture turned from orange into green via dull red. Workup of it after treatment with sodium perchlorate[4] gave **3** as a green powder in 15% isolated yield. Electro-oxidation of **3** (at +1.1 V vs SCE in dichloromethane) produced a black film, different in electrical and electrochemical properties from the reported films[2] of polypyrrole obtained by direct electro-oxidation of **2** (Scheme 1). For example, the cyclic voltammogram of the black film[5] in a $Et_4N^+ClO_4^-$ (0.08 M)/dichloromethane system exhibited unique cation-doping and dedoping waves at ca. −1.2 and +0.2 V vs SCE, respectively, which can never be observed in the voltammogram of conventional polypyrrole.

Scheme 1. Electrochemical Formation of Polypyrrole Films under Two Different Conditions



The ionic structure of **3** possessing a highly conjugated system was suggested by its UV−vis spectrum (in CH_3CN) [λ_{max} (ϵ) 280 (11500), 368 (13500), 477 (15900), 611 nm (7100)]. **3** was stable at low temperatures in a limited range of solvents such as acetone and CH_3CN (no decomposition at 0 °C; $t_{1/2}$ = 20 h at 20 °C; $t_{1/2}$ = 5 h at 40 °C in acetone).[6] A single peak at *m*/*z* 381 in the negative electron spray ionization (ESI) MS[7] of **3** suggested an adduct composed of **1** (MW: 315) and **2** (MW: 67). The ^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra in acetone-d_6 at 0 °C indicated that **3** was a 9:2 mixture[8] of isomeric compounds (the major isomer **3a**, and the minor isomer **3b**). Characteristic signals at δ_C 50.31 and δ_C 56.15 in the ^{13}C NMR spectrum due to aliphatic methine carbons were found to be linked to protons at δ_H 6.53 and δ_H 7.06 in the ^1H NMR spectrum with a long-range coupling (J = ca. 1.0 Hz), respectively, by the $^1H-^{13}C$ HMQC experiment, suggesting the possibility of the products as Meisenheimer complexes.[9] Cross-peaks in the $^1H-^{13}C$ HMBC[10] and in the $^1H-^{15}N$ HMBC[11] experiments supported that **3a** and **3b** were such complexes carrying a pyrrole unit attached at the 3 and 1 positions of the trinitrofluorenone component. On the other hand, positive ESIMS[7] of **3** showed three characteristic peaks at *m*/*z* 64, 105, and 146 corresponding to $[(CH_3CN)Na]^+$, $[(CH_3CN)_2Na]^+$, and $[(CH_3CN)_3Na]^+$, indicating the presence of a sodium ion (Na^+)[12] in **3** as a countercation. Thus, **3** was established to be an inseparable 9:2 mixture of sodium salts[13] of isomeric Meisenheimer complexes of **1** and **2**, in which the addition reaction occurred mainly at the 3 position of **1** (Figure 1).

No reaction occurred under either nonelectrochemical or only one-electron reduction (−0.6 V vs SCE) conditions. Additionally, starting materials were completely recovered when **2** was treated with a dianion $\mathbf{1}^{2-}$ independently prepared from **1**. Thus, the complex **3** appears to be the

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(2) (a) Diaz, A. F.; Kanazawa, K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635−636. (b) Kanazawa, K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A. *Ibid.* **1979**, 854−855.

(3) Gill, W. D. *J. Appl. Phys.* **1972**, *43*, 5033−5040.

(4) In a preliminary experiment we observed that the product tended to incorporate Na^+ during purification by column chromatography (SiO_2) using Wakogel C-100, which is known to contain a small amount of Na^+. Workup was carried out as follows: After evaporation of the solvent followed by washing with diethyl ether, the residue was passed through a short SiO_2 column chromatography eluting with acetone−hexane (1:1) to remove highly polar red-colored material. A slight excess of $NaClO_4$ was added to a solution of the crude product in acetone−hexane (3:1), and then the mixture was purified by SiO_2 column chromatography to give **3**.

(5) Characterization of the new film will be discussed elswhere.

(6) The changes in the absorption maxima in the UV−vis spectra were followed with time. The values of $t_{1/2}$ in DMSO and in MeOH at 20 °C were estimated to be 10 and 4 h, respectively, by the same experiment. A powder of **3** could be stored without decomposition at 0 °C in an inert atomosphere.

(7) CH_3CN was used as a solvent for preparation of samples for measurement. The expected peak due to a molecular ion could not be observed in the FABMS of **3**.

(8) Separation of the isomeric products has not been achieved to date.

(9) (a) Halle, J. C.; Terrier, F.; Pouet, M. J.; Simonnin, M. P. *J. Chem. Res. (S)* **1980**, 360−361. (b) Sepuleri, P.; Goumont, R.; Halle, J.-C.; Buncel, E.; Terrier, F. *J. Chem. Soc., Chem. Commun.* **1997**, 789−790.

(10) Selected assignment of the cross-peaks as follows: [**3a**: δ_H 6.67 (C_α-H)−δ_C 56.15 (C_3), δ_H 7.06 (C_3-H)−δ_C 120.86 (C_α), δ_H 7.06 (C_3-H)−δ_C 125.56 (C_1), δ_H 7.06 (C_3-H)−δ_C 133.02 (C_{4a}), δ_H 8.12 (C_1-H)−δ_C 56.15 (C_3), δ_H 8.12 (C_1-H)−δ_C 133.02 (C_{4a}), δ_H 8.12 (C_1-H)−δ_C 184.62 (C_9); **3b**: δ_H 6.68 (C_α-H)−δ_C 50.31 (C_1), δ_H 6.53 (C_1-H)−δ_C 120.02 (C_α), δ_H 6.53 (C_1-H)−δ_C 130.92 (C_3), δ_H 6.53 (C_1-H)−δ_C 145.02 (C_{4a}), δ_H 6.53 (C_1-H)−δ_C 188.88 (C_9), δ_H 8.82 (C_3-H)−δ_C 145.02 (C_{4a})].

(11) Nitromethane in acetone was referenced to 0 ppm as an external standard. Selected assignment of cross-peaks as follows: [**3a**: δ_H 7.06 (C_3-H)−δ_N −11 (C_2−N), δ_H 8.12 (C_1-H)−δ_N −11 (C_2−N); **3b**: δ_H 8.82 (C_3-H)−δ_N −10 (C_2−N)], while no cross-peak between C_1-H and C_2−N in the minor isomer **3b** was observed.

(12) A signal due to Na^+ was observed at δ −7.50 in the ^{23}Na NMR (in CH_3CN-d_3), where NaCl in D_2O was referenced to 0 ppm as an external standard.

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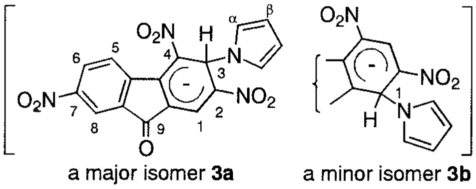


Figure 1. An inseparable mixture of Meisenheimer complexes **3**.

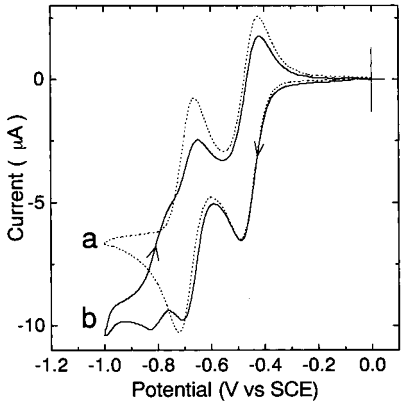
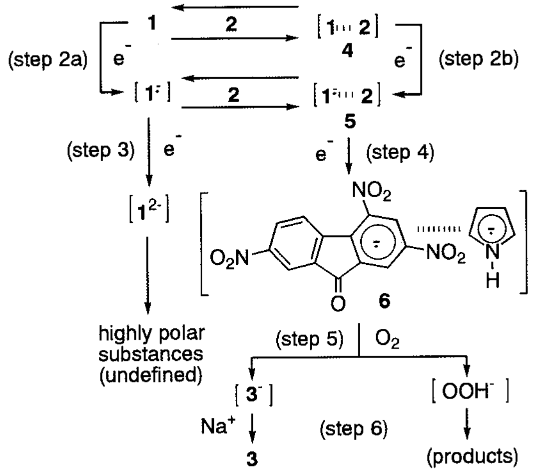


Figure 2. Cyclic voltammograms of (a) **1** in the absence of **2** and (b) **1** in the presence of **2** in CH_3CN (2.0 mM) containing 0.1 M $Et_4N^+ClO_4^-$. Scanning rate = 20 mV s^{-1}.

result of two-electron transfer occurring after complexation of **1** and **2**. Lack of N-substitution of the pyrrole component was shown to be a prerequisite for the formation of **3**, because indole and carbazole gave green adducts[14] with similar absorption spectra to that of **3**, but no generation of a green analogue of **3** was observed with *N*-methylpyrrole in place of **2**. Furthermore, we observed that the dull-red color was maintained during the whole period of reaction (>27 h) when N_2 was continuously bubbled into the solution throughout the electroreduction, while the reaction mixture immediately became green under aerobic conditions. The dull-red solution in the former case dramatically turned green on exposure to air. Isolation of the same green adduct **3** in each case showed the crucial role of O_2 in the product formation.[15]

These experimental data could lead us to speculate as to the mechanism of the electrochemical formation of Meisenheimer complex **3** (Scheme 2), in which (i) **1** interacts with **2** to form a complex **4** in equilibrium (step 1), (ii) a stepwise reduction of **1** yields a radical anion $\mathbf{1}^{\bullet-}$ (step 2a) and a dianion $\mathbf{1}^{2-}$ (step 3),[16] (iii) direct one-electron transfer to **4** gives a complex radical anion **5** (step 2b), which can be indirectly produced by complexation between $\mathbf{1}^{\bullet-}$ and **2**, (iv) **2** itself is not reduced under this condition. However, $\mathbf{1}^{\bullet-}$ in species **5** is expected to be similar to $\mathbf{1}^{2-}$ due to donation of electrons of **2** to $\mathbf{1}^{\bullet-}$. Thus, the second electron would be transferred to the resultant electron-withdrawn pyrrole unit to produce a double radical anion **6** (step 4), (v) O_2 is known to act as a radical scavenger.[17] Therefore, attack of O_2 to the hydrogen atom of an activated pyrrole with radical character as in **6** causes collapse into an anionic σ-complex $\mathbf{3}^-$ and hydroperoxide anion (step 5), and (vi) $\mathbf{3}^-$ is finally stabilized by incorporation of Na^+ (step 6).[18]

Scheme 2. A Proposed Mechanism for the Electroreductive Production of Meisenheimer Complex 3



A cyclic voltammetric study on the electrochemical reaction seems to support the proposed mechanism. The cyclic voltammogram of **1** in CH_3CN showed two well-defined reduction waves with half-wave potentials of −0.49 V and −0.73 V vs a SCE (curve a in Figure 2) due to the formation[19] of a radical anion $\mathbf{1}^{\bullet-}$ and a dianion $\mathbf{1}^{2-}$, respectively. On the other hand, an additional third wave (−0.84 V vs SCE), attributable to the formation of a complex double radical anion **6**, was observed in that measure on the reaction mixture (curve b in Figure 2).

In conclusion, the electroreduction of pyrrole (**2**) in the presence of TNF **1** results in the formation of an isolable Meisenheimer complex **3**, which could be produced by action of O_2 to a complex radical anion **6**. Anionic σ-complexes are generated by strong interaction of electron-deficient aromatics such as **1** with nucleophiles.[20] Nitrogen bases which do result in formation of complexes have previously been limited to either aliphatic primary or secondary amines or amide bases.[9a] Therefore, this is the first isolation[21] of a Meisenheimer complex with a nonnucleophilic pyrrole molecule produced under an electrochemical (nonbasic) condition.

Supporting Information Available: 1D (^1H and ^{13}C) and 2D ($^1H-^{13}C$ HMQC, $^1H-^{13}C$ HMBC, and $^1H-^{15}N$ HMBC) NMR spectra of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Elemental analysis of $C_{17}H_9N_4O_7Na$ as the expected formula of **3** was calculated to be C, 50.50; H, 2.24; N, 13.86; Na, 5.69. The combustion analysis of **3** for C, H, and N using three different instruments gave the average data of C, 48.12; H, 3.14; N, 11.78, and the atomic spectrum of **3** for Na gave 4.44% of Na. The ^1H and ^{13}C NMR spectra of **3** in CH_3CN-d_3 at 0 °C showed the inclusion of nearly one molar ratio of acetone. On the basis of these data, we concluded that **3** was isolated as $C_{17}H_9N_4O_7Na{\cdot}mC_3H_6O{\cdot}nH_2O$ (e.g., calcd for $^1/_3C_{17}H_9N_4O_7Na + {}^2/_3C_{17}H_9N_4O_7Na{\cdot}C_3H_6O{\cdot}2H_2O$: C, 48.96; H, 3.31; N, 12.11; Na, 4.97).

[14] Although attempts to isolate these adducts failed due to their instabilities, successive electro-oxidation under the same condition as with adduct **3** afforded the corresponding new films. Their characterization will be discussed elswhere.

[15] It is inevitable that O_2 will permeate into a cathode compartment from the anode compartment through a sintered glass filter during extended periods of electrolysis even under a nitrogen atmosphere.

[16] Highly polar red coproducts would be derived from dianion $\mathbf{1}^{2-}$.

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[18] Hydroperoxide anion may be scavenged by other species including the solvent.

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[21] Recently a π-complex precursor in Meisenheimer complex formation was isolated in the reaction between trinitrobenzene and sodium indole-3-carboxylate in MeOH.[9b] The π-complex was shown to rapidly give rise to the corresponding σ-complexes, when it was placed in DMSO. The authors pointed out the important role of an increased charge density of an indole nucleus by substitution of a carboxylate ion at the 3 position for these complex formations.