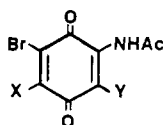


°C for 15 min; the mixture was poured into 150 mL of H₂O and filtered to give a crude product which was a mixture of N-acylated and O,N-diacetylated 13. This mixture was stirred with 300 mL of 5:1 MeOH/H₂O, and 100 mL of saturated aqueous NaHCO₃ was added. After being stirred at 20 °C for 15 min, the mixture was acidified with 2.5 M HCl, and the precipitate was filtered and washed with water to give 7.88 g (83%) of 14 which was used directly. A sample recrystallized from aqueous MeOH melted at 179 °C (lit.^{11b} mp 178 °C).

2-Acetamido-6-bromobenzoquinone (2). Phenol 14 (692 mg, 2.24 mmol) was dissolved in 23 mL of acetic acid. A solution of 3.70 g (6.75 mmol) of ceric ammonium nitrate in 23 mL of H₂O was added portionwise over 2 min, and the solution was stirred at 20 °C for 10 min. The mixture was poured into 200 mL of H₂O and extracted with AcOEt (2 × 200 mL); the organic extracts were washed with water (3 × 100 mL), dried (Na₂SO₄), and evaporated to give 366 mg of pure quinone (67%). Recrystallization from benzene gave analytically pure material as yellow-orange crystals: mp 159–160 °C; ¹H NMR (CDCl₃/Me₂SO-*d*₆) 9.10 (1 H, br s), 7.55 (1 H, d, *J* = 2.3 Hz), 7.17 (1 H, d, *J* = 2.3 Hz), 2.23 (3 H, s); IR (Nujol) 3280, 1716, 1684, 1639, 1625–1600, 1525–1500 cm⁻¹. Anal. Calcd for C₈H₆BrNO₃: C, 39.37; H, 2.48. Found: C, 39.58; H, 2.48.

Longer reaction times in HOAc or the use of CH₃CN as a solvent gave a dibromoquinone assigned¹⁵ structure 15: yellow



15, X = Br, Y = H
16, X = H, Y = Br

crystals; mp 198–200 °C (from benzene); ¹H NMR (CDCl₃) 7.43 (s, 1 H), 7.4 (br s, 1 H), 2.24 (s, 3 H); IR (Nujol) 3305, 1698, 1680, 1660, 1655, 1627, 1594 cm⁻¹. Anal. Calcd for C₈H₅Br₂NO₃: C, 29.75; H, 1.56. Found: C, 29.75; H, 1.51.

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Registry No. 1, 87013-11-4; 2, 87013-12-5; 3, 38847-62-0; 4, 2072-09-5; 5, 609-89-2; 6, 527-62-8; 7, 55202-45-4; 8, 2072-30-2; 12, 15969-09-2; 13, 10539-14-7; 14, 55202-09-0.

(15) Structure 15 is preferred over 16 on the basis of mechanistic considerations; it is also in accord with the chemical shift observed for the nuclear proton.

The Two Hydrogen-Oxygen Bond-Dissociation Energies of Hydroquinone

Louis E. Friedrich

Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650

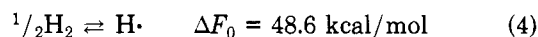
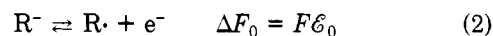
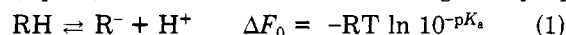
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There are few experimental determinations of the first bond-dissociation energy (BDE) of hydroquinone. The most recent determination was by Mahoney,¹ who concluded that the first BDE for this most important hydrogen-transfer agent is 85 kcal/mol. There are no literature reports for the second BDE of hydroquinone.

A variety of methods exist to determine hydrogen bond-dissociation energies (BDEs). These methods have been reviewed periodically² and include equilibrium

methods, kinetic methods, electron-impact studies, spectroscopic determinations, chemical activation, and theoretical calculations. The uncertainty in BDEs is ±2–5 kcal/mol.

For those weak acids whose pK_as can be determined and whose conjugate bases can be reversibly oxidized to their neutral radicals, a simple thermodynamic cycle can be constructed that leads to the free energy of bond dissociation (eq 1–4). The sum of the reactions is given by eq



5. For some purposes, the free energy of bond dissociation



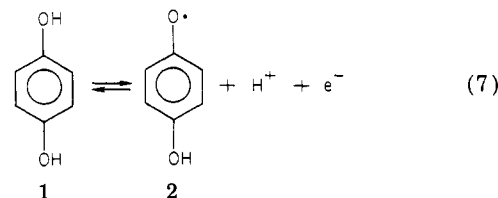
$$\Delta F_0 = 2.303RT(\text{p}K_a) + F\mathcal{E}_0 + 48.6 \text{ kcal/mol}$$

is the desired quantity, but formally, the BDE is an enthalpic quantity. For medium to large molecules, the entropies of RH and R[·] are approximately equal at 25 °C. The major TΔS₀ correction is due to H[·], which at 25 °C is 8.2 kcal/mol.³ Therefore

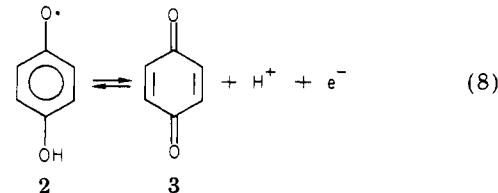
$$\text{BDE}(25 \text{ }^\circ\text{C}) \approx 1.36\text{p}K_a + 23.1\mathcal{E}_0 + 56.8 \text{ kcal/mol} \quad (6)$$

This electrochemical-acidity method is not new. Breslow⁴ has used electrochemistry extensively and has determined the relative carbon-oxygen BDEs of several alcohols. Most important, Brauman has applied the method in the gas phase to determine the bond-dissociation energy of several species.⁵ But this method has not been used with readily available solution-phase pK_a and electrochemical data.

As applied to hydroquinone, the published half-cell reactions in water are⁶ as shown in eq 7 and 8. The pK_as



$$\Delta F_0 = 23.1 \times 1.084 \text{ kcal/mol}$$



$$\Delta F_0 = 23.1 \times 0.326 \text{ kcal/mol}$$

are included in the published \mathcal{E}_0 s so that only the free energy and entropy of formation for H[·] need to be added to obtain the BDEs.⁷ The first and second BDEs for 1

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and **2** are calculated to be 82 and 64 kcal/mol, respectively, with a propagated error of probably less than 1 kcal/mol.

The method can also be used for solution-phase anion oxidations that are not fully reversible, although only an inequality for the BDE can be calculated. For example, phenol has a pK_a of 10.0 and a literature $E_{p/2}$ of 0.48 V (vs. NHE) in water at pH 13.⁸ The calculated BDE is ≥ 87 kcal/mol, whereas the accepted value seems to be ~ 85 kcal/mol^{2c} but ranges from 80 to 88 kcal/mol.⁹ The fact that the calculated BDE for phenol is near the upper range of the literature values may be due to the inequality, but Breslow has shown that even poorly behaved cyclic voltammetric measurements are likely to be reasonable approximations of reversible potentials.⁴ Also, the calculated BDE by this method may be affected by hydrogen bonding effects with the solvent (water).

Acknowledgment. Thanks to Dr. Eric Brown for many helpful discussions.

Registry No. Hydroquinone, 123-31-9.

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Organic Metals. Preparation and Properties of 7,7,8,8-Tetracyano-*p*-quinodimethaneacetic and -propanoic Acids

Jamil Baghdadchi and Charles A. Panetta*

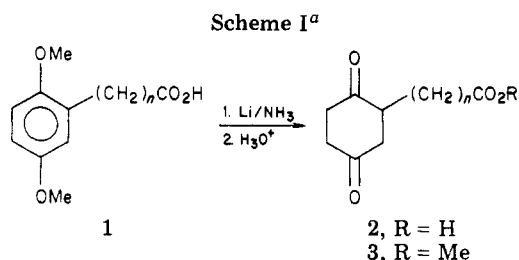
Department of Chemistry, University of Mississippi,
University, Mississippi 38677

Received April 20, 1983

In recent years, some attention has been focused on organic metals: solid carbon compounds with interesting electrical properties.¹ The charge-transfer (CT) complex between the electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)² and the electron donor tetrathiafulvalene (TTF)³ is probably the best known and most widely investigated example of an organic metal.⁴

Many derivatives⁵ of TCNQ have been prepared in efforts to improve the metallic character of the CT salts and to better understand the electron transport properties of these systems. As far as we could determine, none of the above derivatives included the carboxyl-type moiety which we required for a related research project.

7,7,8,8-Tetracyano-*p*-quinodimethaneacetic (**6a**) and -propanoic acids (**6b**) were prepared from commercially available (2,5-dimethoxyphenyl)acetic and -cinnamic acids,



^a a, n = 1; b, n = 2.

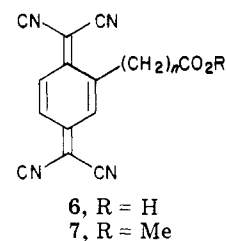
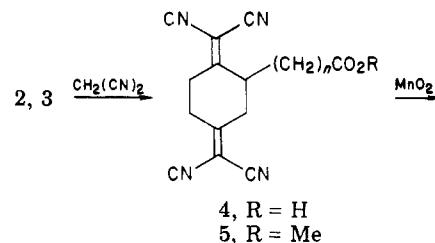


Table I. Half-Wave Reduction Potentials^a

	TCNQ ^b	Me-TCNQ ^b	6a	6b
$E_{1/2}^1$	0.190	0.170	0.236	0.222
$E_{1/2}^2$	-0.350	-0.340	-0.267	-0.275

^a In volts vs. SCE as determined by cyclic voltammetry at a Pt-button electrode in acetonitrile, *n*-Bu₄N·ClO₄, or *n*-Bu₄N·BF₄, (0.1 M). ^b Data from ref 5b.

Table II. Room-Temperature Conductivities ($\Omega^{-1} \text{ cm}^{-1}$) of TTF Complexes

TTF complexes	conductivity
TCNQ	1-3 ^{a, b}
Me-TCNQ	500 ^{b, c}
6a	1 ^a
6b	1 ^a

^a Compacted pellet. ^b From ref 5b. ^c Single crystal.

respectively. An outline of most of the synthetic steps is presented in Scheme I.

The overall yield of **6a** from **1a** was approximately 4% and that of **6b** from 2,5-dimethoxycinnamic acid was about 18%. The last step, which involved the dehydrogenation of **4**, was chiefly responsible for the low overall yields. In the acetic acid series, these were improved to about 13% by the utilization of methyl esters (**1a** → **2a** → **3a** → **5a** → **7a** or **1a** → **2a** → **4a** → **5a** → **7a**).

The relative electron accepting abilities of TCNQ, Me-TCNQ, **6a**, and **6b** were determined by measuring the reduction potentials of the last two products and comparing these to the reported^{5b} values of the first two (Table I). Both **6a** and **6b** are better electron acceptors than either Me-TCNQ or TCNQ itself. The cyclic voltammograms of **6a** and **6b** showed two reversible one-electron reduction waves (Figure 1 in the supplementary material; see the paragraph at the end of the paper).

Since the new products exhibit reversible electrochemical reduction at potentials more positive than the parent compound, charge-transfer complexes between each of

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