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Proton-Induced Disproportionation of Superoxide Ion in Aprotic Media

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Abstract: The proton-induced disproportionation of superoxide ion (O_2^-) in dimethylformamide and in acetonitrile has been studied by stopped-flow spectrophotometry, cyclic voltammetry, and controlled-potential voltammetry at a rotating-disk electrode. For strongly acidic substrates ($HClO_4$, HCl, and NH_4ClO_4) the disproprotionation reaction is second order with respect to O_2^-, but too rapid to measure accurately, $k > 10^7$ M^{-1} s^{-1}. With less protic substrates (ascorbic acid, phenols, catechols, alcohols, and water) the rate of disproportionation is first order with respect to O_2^- and with respect to substrate; proton transfer is the rate-limiting step. In dimethylformamide the second-order rate constants range from $k = 2 \times 10^4$ M^{-1} s^{-1} for ascorbic acid to $k = 1 \times 10^{-3}$ for water. On the basis of the kinetic data, a self-consistent mechanism for superoxide disproportionation by acidic substrates in nonaqueous solvents is proposed.

The dynamics for the hydrolysis and disproportionation of superoxide (O_2^-) in aqueous media have been characterized in detail by pulse radiolysis.[1-5] For all conditions, the rate-limiting step is second order in O_2^- concentration. The maximum rate occurs at a pH that is equivalent to the pK_a for $HO_2\cdot$; it decreases monotonically with further decreases in the hydrogen ion concentration.

$$O_2^- + H^+ \rightleftharpoons HO_2\cdot \qquad K_{diss} = 2.0 \times 10^{-5} \qquad (1)$$

$$HO_2\cdot + O_2^- \xrightarrow{H^+} H_2O_2 + O_2 \qquad k_2 = 1.0 \times 10^8\ M^{-1}\ s^{-1} \qquad (2)$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad k_3 = 8.6 \times 10^5\ M^{-1}\ s^{-1} \qquad (3)$$

$$O_2^- + O_2^- + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^- \qquad k_4 < 0.3\ M^{-1}\ s^{-1} \qquad (4)$$

At pH 7 the disproportionation equilibrium is far to the right[6]

$$2O_2^- + 2H^+ \rightleftharpoons H_2O_2 + O_2 \qquad K = 4 \times 10^{20} \qquad (5)$$

and even at pH 14 it is complete

$$2O_2^- + H_2O \rightleftharpoons HO_2^- + OH^- + O_2 \qquad K = 9.1 \times 10^8 \qquad (6)$$

Hence, O_2^- has a strong tendency to remove protons from substrates as weakly acidic as water (pK_a = 15,7) and thereby exhibits the characteristics of a Brønsted base. The acid-base equilibrium is driven by its proton-dependent disproportionation (eq 6) rather than by the hydrolysis reaction of eq 1.

A previous study[7] has demonstrated that O_2^- in aprotic media (where it is stable) is disproportionated by the presence of protic substrates such as catechols, ascorbic acid, and α-tocopherol. These processes confirm that O_2^- acts as a strong Brønsted base in aprotic solvents via proton transfer.

Stable solutions of O_2^- in aprotic media can be prepared by controlled-potential reduction of O_2[8,9] or by the dissolution of tetramethylammonium superoxide ($TMAO_2$).[10] The present study has been directed to the characterization of the proton-induced disproportionation of O_2^- by protic substrates in aprotic solvents. The substrates include strong acids ($HClO_4$, HCl, NH_4ClO_4), moderate acids (phenols and catechols), and weak acids (water and 1-butanol),

Experimental Section

Instrumentation. Either a three-electrode potentiostat-amperostat constructed with operational amplifiers[11] or a Princeton Applied Research Model 173/175/179 potentiostat-galvanostat was used for the cyclic voltammetric experiments. The voltammograms were recorded with a Houston Instruments Omnigraph X-Y recorder. The controlled-potential electrolysis experiments were accomplished either with a Wenking Model 61RH potentiostat or with a Princeton Applied Research Model 175 potentiostat-galvanostat and a Princeton Applied Research Model 179 digital coulometer.

For the cyclic voltammetric experiments, the working electrode was a Beckman platinum inlay electrode (No. 39273) which had a surface area of 0.23 cm^2. The auxiliary electrode was a platinum flag electrode which was isolated from the bulk solution by a fine or a medium-porosity glass frit. The reference electrode was a Ag|AgCl (aqueous tetramethylammonium chloride) cracked glass-bead electrode which was adjusted to 0.000 V vs. SCE.[11] The reference electrode was located inside a Luggin capillary (filled with solvent solution) in the cell assembly.

For the controlled-potential electrolysis experiments, a cylindrical platinum mesh electrode was used as the working electrode. A Beckman Model 1855 rotating-disk electrode (Pt; area, 0.34 cm^2) and assembly in conjunction with a potentiostat was used for the study of initial rates of reaction.

A Durrum-Gibson Model D-110 (Durrum Instrument Corp.) stopped-flow spectrophotometer was used for fast-kinetic analyses. The system included a three-reservoir syringe valve block with a mixing dead time of about 2 ms; the temperature was controlled at 25 °C. Two 2-mL syringes were used with a manual pushing block. For measurements of O_2^- in acetonitrile a wavelength of 250 nm was used; for dimethylformamide solutions a wavelength of 300 nm was used.

Chemicals and Reagents. Burdick and Jackson "distilled in glass" acetonitrile (MeCN) and dimethylformamide (DMF) were obtained in quart bottles to minimize contamination by water. The water content as specified by the manufacturer was 0.008% to 0.022%. The solvents were treated with activated Matheson Coleman and Bell Type 4A molecular sieves just prior to their use. Tetraethylammonium perchlorate (TEAP) and ammonium perchlorate (from G. Frederick Smith) were dried in vacuo at 110 °C. Perchloric acid and phenol were obtained from Mallinckrodt, Inc., *n*-butyl alcohol from Eastman Organic Chemicals, and 3,5-di-*tert*-butylcatechol (DTBC), *p*-chlorophenol, *p*-cresol, and *p*-ethoxyphenol from Aldrich Chemical Co. Catechol, L-(+)-ascorbic acid, and *p*-*tert*-butylphenol were obtained from Matheson Coleman and Bell; α-tocopherol was purchased from Calbiochem. High-purity argon

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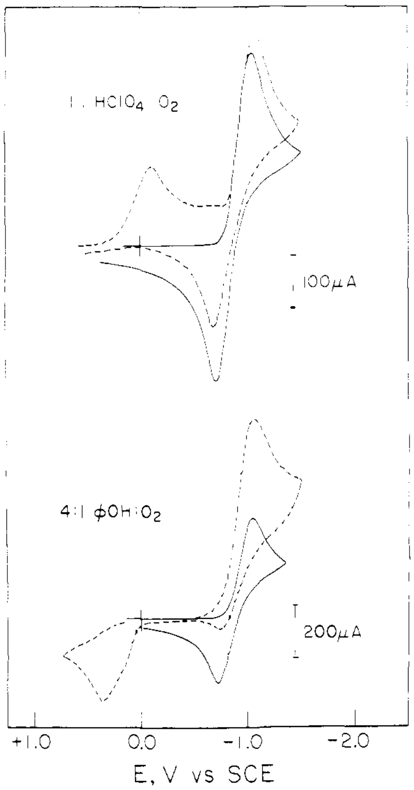

Figure 1. Cyclic voltammograms in dimethylformamide (0.1 M tetraethylammonium perchlorate) of (a) 4.8 mM O_2 (—); (b) 4.8 mM O_2 plus 4.8 mM $HClO_4$ (---); and (c) 4.8 mM O_2 plus 19.2 mM phenol (- - -). Measurements were made with a platinum electrode (area, 0.23 cm^2) at a scan rate of 0.1 V s^{-1}; temperature, 25 °C. $E_{NHE} = E_{SCE} + 0.25$ V.

and oxygen were supplied by the Chemetron Corp. The remaining chemicals were reagent grade and were used without further purification.

Superoxide ion was generated by the electrochemical reduction (at −1.0 V vs. SCE) of a solution through which oxygen (at 1 atm) was continuously bubbled. All electrochemical solutions contained 0.1 M TEAP as the supporting electrolyte. Upon completion of the electrolysis the superoxide solution was degassed with argon to remove any residual oxygen. The concentration of superoxide ion was monitored by cyclic voltammetry with the anodic peak current measured at −0.7 V vs. SCE. Standardization of the current relative to the concentration of superoxide ion was accomplished by controlled-potential coulometric analysis.

Results

Figure 1 illustrates the cyclic voltammetry of O_2 in DMF as well as the effect of a proton source ($HClO_4$ and phenol) on the reduction process. With a 1:1 mol ratio of $HClO_4$-to-O_2 an apparent one-electron reduction occurs at −0.13 V vs. SCE. The assumed product, $HO_2\cdot$, must rapidly disproportionate to H_2O_2 and O_2 to account for this one-electron stoichiometry, the absence of a reverse wave, the limited decrease of the O_2/O_2^- peak height, and the depletion of free protons. In the case of phenol, increasing mol ratios (relative to O_2) cause the reduction of O_2 to shift from a one-electron process to an overall two-electron process. Table I summarizes additional data for the effect of several other acidic substrates upon the reduction potential and overall electron stoichiometry for oxygen in DMF. These observations are consistent with the conclusion that protons induce the disproportionation to O_2 and H_2O_2 of the superoxide ion that results from the electrochemical reduction of oxygen.

Strong Acids. When O_2^- solutions ($TMAO_2$ in DMF or MeCN) are combined with an excess of a strong acid ($HClO_4$, HCl, or NH_4ClO_4) in the same solvent, the rate of disproportionation is so rapid that accurate measurements by the stopped-flow spectrophotometric technique are precluded. However, the combination of HCl (0.2 mM) with an excess of O_2^-, both in MeCN, yields a decay curve that is consistent with a process that is second order in $HO_2\cdot$. The average of the data for five separate runs yields a second-order rate constant of (5 ± 1) × 10^6 M^{-1} s^{-1} for the disproportionation reaction. With excess $HClO_4$ and NH_4ClO_4 the decay rates for O_2^- (as $HO_2\cdot$) are too fast to measure within the experimental conditions, $k > 10^7$ M^{-1} s^{-1}.

Table I. Half-Peak Potentials and Electron Stoichiometry for the Reduction of 4.8 mM O_2 in DMF (0.1 M TEAP) in the Presence of a Fivefold Excess of Acidic Substrate

substrate	$(E_{pc})_{1/2}$ V vs. SCE	$n(e^-/O_2)$
ascorbic acid	−0.73	2
3,5-di-*tert*-butylcatechol	−0.85	2
phenol	−0.88	2
α-tocopherol	−0.88	2
H_2O	−0.90	1
1-butanol	−0.90	1
none	−0.90	1

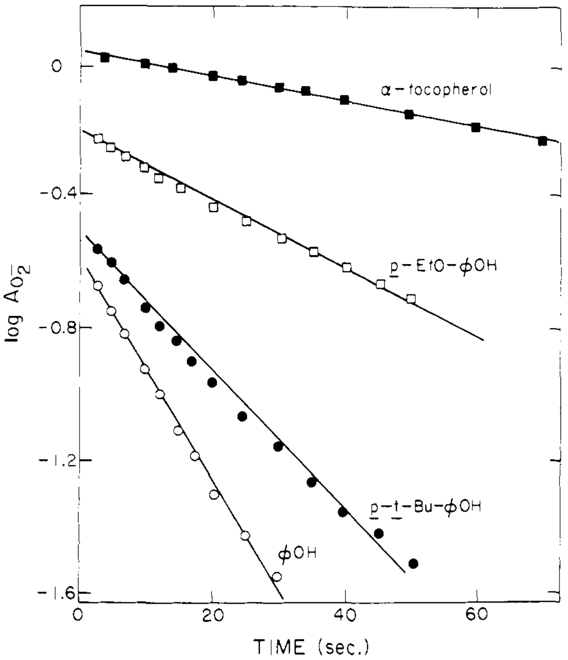

Figure 2. Rates of disappearance of 1 mM O_2^- in the presence of various protic substrates in dimethylformamide at 25 °C: (○) 0.01 M phenol; (●) 0.02 M *p*-*tert*-butylphenol; (□) 0.01 M *p*-ethoxyphenol; (■) 0.02 M α-tocopherol. Absorbance of O_2^- monitored by stopped-flow spectrophotometry at 300 nm.

Combination of 2 equiv of O_2^- with 1 equiv of $HClO_4$ (both in DMF) results in the disproportionation of one-half of the O_2^-.

Moderate Acids. The kinetics for the disproportionation of stable O_2^- solutions in DMF by moderately strong protic substrates (ascorbic acid, phenols, and catechols) has been studied by stopped-flow spectrophotometry. Figure 2 illustrates the pseudo-first-order decay of O_2^- when it is combined with an excess of several protic substrates in dimethylformamide. Because the initial proton transfer and disproportionation steps are followed by a number of secondary reactions, the initial rates have been used to evaluate the pseudo-first-order rate constants. Variation of substrate concentration confirms that the rate for the disproportionation process is first order in substrate. Analogous results are obtained when phenol and α-tocopherol are studied in acetonitrile.

For the slower reactions the decay of O_2^- also has been monitored by controlled-potential voltammetry (with a platinum rotating-disk electrode). At potentials more positive than −0.62 V vs. SCE the anodic current provides a direct measure of the superoxide ion concentration.

The second-order rate constants for the disproportionation of O_2^- in the presence of this group of substrates are summarized

Table II. Observed Rate Constants for the Disproportionation of O_2^- in the Presence of Excess Substrate (HA) at 25 °C in Dimethylformamide[a]

substrate (HA)	k, M^{-1} s^{-1}	pK_a[e]
NH_4ClO_4	$\gg 1 \times 10^5$	8.5
ascorbic acid (H_2Asc)	2×10^4	10.5
$HAsc^-$ [b]	8×10^1	30.3
phenol	1×10^4	19.8
	1×10^4 [d]	
p-chlorophenol	6×10^3	
p-*tert*-butylphenol	5×10^3	
p-ethoxyphenol	5×10^3	
p-creosol	6×10^3	
α-tocopherol	8×10^2	28.4
	6×10^2 [d]	
catechol	7×10^3	
3,5-di-*tert*-butylcatechol ($DTBCH_2$)	1×10^4	19.9
$DTBCH^-$ [b]	5×10^2	28.2
H_2O [c]	1×10^{-3}	32.6
1-butanol[c]	1×10^{-3}	33.3

[a] Decay of O_2^- in the presence of at least a tenfold excess of substrate monitored by stopped-flow spectrophotometry. [b] Decay of O_2^- monitored by rotating disk electrode voltammetry at −0.62 V vs. SCE, 0.1 M TEAP in DMF. [c] Decay of O_2^- monitored by periodic anodic voltammetry at a scan rate of 0.1 V s^{-1}; 0.1 M TEAP in DMF. [d] In acetonitrile. [e] Reference 6.

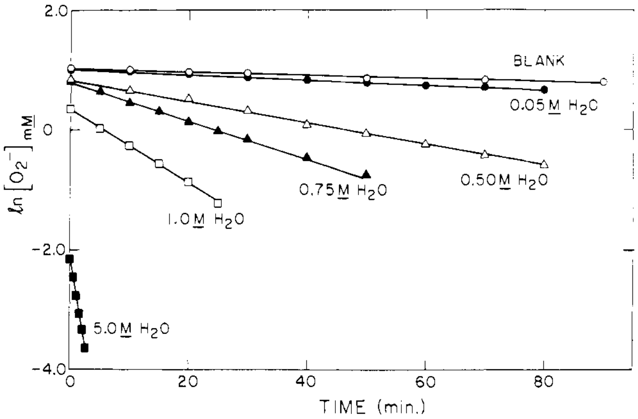

Figure 3. Rates of disappearance of 3 mM O_2^- in the presence of various concentrations of water in dimethylformamide at 25 °C. Concentration of O_2^- monitored by periodic voltammetric scans at a platinum electrode (area, 0.23 cm^2); anodic scan rate, 0.1 V s^{-1}.

in Table II. The effective pK_a' values for several of the substrates[7] also are tabulated.

Weak Acids. Figure 3 illustrates the rate of decay for O_2^- in DMF in the presence of large excesses of water. The O_2^- concentration has been measured by periodic voltammetric scans. Again, the rate of disproportionation is first order in O_2^- and in substrate. The second-order rate constants for 1 M substrate concentrations in DMF are summarized in Table II. As the concentration of H_2O in DMF is increased, the effective second-order rate constant increases (Table III). The presence of an equimolar amount of base (tetraethylammonium hydroxide) relative to H_2O does not significantly affect the rate constant for the water-induced disproportionation of O_2^-. Both of these observations indicate that the protic strength (effective pK_a') of H_2O has a direct influence on the observed rates.

Discussion and Conclusions

Strong Acids. When O_2^- is combined with an excess of a strongly protic substrate ($HClO_4$, HCl, or NH_4ClO_4) in an aprotic solvent, protonation occurs at a diffusion-controlled rate

$$H^+ + O_2^- \overset{k_7}{\rightleftharpoons} HO_2\cdot \qquad K_7 = 10^{12} \tag{7}$$

Reference to Figure 1a indicates that the reduction potential for the O_2/O_2^- couple is shifted by +0.72 V in the presence of $HClO_4$. Hence, a reasonable estimate of the pK_a value for $HO_2\cdot$ in DMF is 12 ($pK_a = \Delta E°'/0.059$); this is the basis for the value assigned to K_7.

Table III. Observed Rate Constants for the Disproportionation of O_2^- in the Presence of Excess H_2O at 25 °C in Dimethylformamide (0.1 M Tetraethylammonium Perchlorate)

initial concn				
O_2^- (mM)	H_2O (M)	pK_a'	k_1', s^{-1}	k_2,[b] M^{-1} s^{-1}
2.78	0.00		3.8×10^{-5} (blank)	
2.96	0.05	32.4	6.9×10^{-5}	6.2×10^{-4}
2.88	0.50		3.0×10^{-4}	5.2×10^{-4}
2.97	0.75		5.3×10^{-4}	6.5×10^{-4}
2.78[a]	1.00	25.3	1.0×10^{-3}	9.8×10^{-4}
2.40[a]	5.00		1.0×10^{-2}	2.0×10^{-3}

[a] Measured by rotating disk voltammetry; others measured by cyclic voltammetry. [b] $k_2 = (k_1' - k_1'_{(\mathrm{blank})})/[H_2O]$.

If rapid protonation of O_2^- is assumed (analogous to the diffusion-controlled process in aqueous media (eq 3), then the rate-limiting step becomes the bimolecular disproportionation of $HO_2\cdot$. The stopped-flow studies for O_2^- plus excess $HClO_4$ in DMF and MeCN indicate that this process is too fast to measure,

$$HO_2\cdot + HO_2\cdot \overset{k_8}{\rightleftharpoons} H_2O_2 + O_2 \qquad K_8 = 10^{25} \tag{8}$$

with $k_8 > 10^7$ M^{-1} s^{-1}. This is more than an order of magnitude greater than the value for aqueous media,[1] which may be the result of weaker solvation of $HO_2\cdot$ by MeCN or DMF. Weaker solvation would facilitate the transfer of a hydrogen atom from one $HO_2\cdot$ to another.

The redox data for $O_2/HO_2\cdot/H_2O_2$ in aqueous 1 M $HClO_4$,[6,12] $O_2 + H^+ + e^- \rightarrow HO_2\cdot$ ($E°'$, −0.05 V vs. NHE) and $HO_2\cdot + H^+ + e^- \rightarrow H_2O_2$ ($E°'$, +1.44 V), have been used to evaluate K_8 ($\log K = \Delta E°'/0.059$). We have assumed that the solvent effects on reaction 8 are minimal and that the value of K_8 for a DMF medium is the same as for aqueous conditions. Combination of reaction 7 and 8 yields an overall disproportionation reaction

$$2H^+ + 2O_2^- \rightleftharpoons H_2O_2 + O_2 \qquad K_9 = 10^{49} \tag{9}$$

In contrast to aqueous conditions, reaction 2 ($HO_2\cdot + O_2^-$) is not competitive in MeCN or DMF. Hence, the combination of two O_2^- ions and one $HClO_4$ is controlled by reactions 7–9.

$$2O_2^- + H^+ \rightarrow \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}O_2 + O_2^- \tag{10}$$

Thus, $HO_2\cdot$ is not a kinetically viable oxidant for O_2^- in aprotic media. Electrochemical measurements (Figure 1) confirm that the lifetime of $HO_2\cdot$ is too short to observe its electron-transfer reduction.

Moderate and Weak Acids. In contrast to strong acids or aqueous conditions, the rate-limiting step for the proton-induced disproportionation of O_2^- in aprotic solvents by moderate or weak protic substrates (HA) is proton transfer (Table II)

$$O_2^- + HA \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} HO_2\cdot + A^- \tag{11}$$

The values for k_{11} for various substrates are summarized in Tables II and III. For example, with phenol (PhOH, pK_a = 20)[7]

$$O_2^- + PhOH \rightleftharpoons HO_2\cdot + PhO^- \qquad K_{12} = K_a/K_7 = 10^{-8} \tag{12}$$

Reference to Table I indicates that for phenol the value of k_{11} is 10^4 M^{-1} s^{-1}. Reaction 12 is driven to completion by the rapid disproportionation of $HO_2\cdot$ (reaction 8). Because the PhO^- product of reaction 12 is a strong base, it will abstract a proton from H_2O_2 (pK_a 11 in DMF)[7]

$$H_2O_2 + PhO^- \rightleftharpoons PhOH + HO_2^- \qquad K_{13} = k_{H_2O_2}/K_a = 10^9 \tag{13}$$

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Thus, the overall disproportionation process is represented by the summation of two times eq 12 plus eq 8 and eq 13

$$2O_2^- + PhOH \rightleftharpoons HO_2^- + O_2 + PhO^- \qquad K_{14} = K_aK_8K_{H_2O_2}/K_7^2 = 10^{38}K_a = 10^{18} \quad (14)$$

Thus, the reaction is driven far to the right to yield stoichiometric amounts of HO_2^- and PhO^-.

Even weakly protic substrates such as 1-butanol (BuOH) and water induce the complete disproportionation of O_2^- in DMF, but at much reduced rates (Tables II and III). A previous study has determined the apparent pK_a values for BuOH and H_2O in DMF to be approximately equal ($pK_a = 33$).[7] Thus, the overall reactions can be expressed in a form analogous to eq 14,

$$2O_2^- + BuOH \rightleftharpoons HO_2^- + O_2 + BuO^- \qquad K_{15} = 10^5 \quad (15)$$

and

$$2O_2^- + H_2O \rightleftharpoons HO_2^- + O_2 + OH^- \qquad K_{16} = 10^5 \quad (16)$$

For weak acids such as water and alcohols, the overall decomposition of O_2^- is further complicated by the base-induced (A^-) decomposition of H_2O_2 in aprotic solvents.[13]

$$H_2O_2 + A^- \rightarrow HO_2^- + HA \quad (17)$$

$$HO_2^- + H_2O_2 \rightarrow O_2^- + \cdot OH + H_2O \quad (18)$$

The rate of protonation of O_2^- by moderate and weak protic substrates probably depends on the stability of a superoxy intermediate.[14]

$$O_2^- + HA \rightarrow [\cdot O_2{:}H{:}A]^- \rightarrow A^- + HO_2\cdot \quad (19)$$

Although this process is diffusion controlled for strong acids and slow for water and alcohols, with moderate substrates the relative rates appear to depend on steric and electrostatic factors as much as relative pK_a values (Table II).

The first-order dependence on HA concentration for the proton-induced disproportionation of the superoxide ion in aprotic media (eq 11) may be representative of a hydrophobic biological matrix.[12] If so, the effective rate for the nonenzymatically catalyzed disproportionation of superoxide in mitochondria and in erythrocytes would be much slower than the second-order process in bulk water (eq 2 and 3). Hence, the need for superoxide dismutases under such conditions is even more compelling. The latter maintain the free superoxide ion concentration at levels that are several orders of magnitude lower than would be possible if reaction 11 were rate limiting.

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Registry No. O_2^-, 11062-77-4; H_2O, 7732-18-5; NH_4ClO_4, 14452-39-2; H_2Asc, 50-81-7; $HAsc^-$, 299-36-5; $DTBCH_2$, 1020-31-1; $DTBCH^-$, 65767-25-1; phenol, 108-95-2; α-tocopherol, 59-02-9; 1-butanol, 71-36-3; *p*-chlorophenol, 106-48-9; *p*-*tert*-butylphenol, 98-54-4; *p*-ethoxyphenol, 622-62-8; *p*-cresol, 106-44-5; catechol, 120-80-9.

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Ligand Additivity: Applications to the Electrochemistry and Photoelectron Spectroscopy of d^6 Octahedral Complexes

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Abstract: It is proposed that the energies of the three MO's derived from the three metal d_π orbitals in d^6 $ML_nL'_{6-n}$ systems obey the simple additivity relationship $\epsilon = a + bn + cx$, where x is the number of ligands L which can interact with a given d_π orbital, and a, b, and c are empirically determined parameters. This relationship is used to investigate the electrochemical oxidation data for the compounds $M(CO)_n(CNR)_{6-n}$ (M = Mn(I), Cr(0); R = CH_3, C_6H_5). The model fits the data extremely well, and it also explains the different oxidation potentials observed for the isomers with $n = 2$ or 3. Two of the derived parameters are shown to be measures of the difference in the abilities of the ligands to electrostatically stabilize the metal center and the difference in the abilities of the ligands to stabilize d_π orbitals by π back-bonding. It is indicated that, as a ligand for Cr(0), phenyl isocyanide is both a poorer σ donor and poorer π acceptor than methyl isocyanide. The application of the model to the photoelectron spectroscopy of $ML_nL'_{6-n}$ systems is discussed and predictions are made concerning the trends in the ionization potentials of such systems.

The notion that ligand effects upon a transition-metal center are, in some sense, additive has been a cornerstone of intuitive inorganic chemistry. In recent years several groups have attempted to quantify ligand additivity relationships, especially in metal carbonyl complexes and their derivatives, for application to a variety of physical measurements. Timney[1] has extended the ideas of Haas and Sheline[2] to yield a marvelously simple empirical relationship for the prediction of CO stretching frequencies in a wide variety of metal carbonyl complexes. Other groups have attempted to obtain empirical ligand parameters for the correlation of ^{13}C NMR spectra of metal carbonyls.[3] With regard to the energetics of electrons in metal carbonyl complexes, many groups have attempted the quantitative correlation of electrochemical data. Pickett and Pletcher[4] proposed that the oxidation potentials

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