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Use of the Hammett Correlation and σ^+ for Calculation of One-Electron Redox Potentials of Antioxidants

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Spectral, acid–base, and redox properties of methoxyphenoxyl radicals were determined in aqueous solutions by pulse radiolysis. Except for 2,6-dimethoxyphenoxyl, with $\lambda_{max} < 300$ nm, methoxyphenoxyl radicals absorb in the visible spectrum, with high molar absorptivities. From the effect of ionic strength on the rate of radical decay, a $pK_a < 2$ was estimated for the deprotonation of phenolic radical cations. The oxidation potentials of methoxyphenols were determined from the electron-transfer equilibria with inorganic redox standards. The largest effect of methoxy groups on oxidation potential was observed for 2,6-dimethoxyphenol, $E_7 = 0.58$ V vs NHE, whereas the effect of meta substitution was minimal for 3,5-dimethoxyphenol, $E_7 = 0.85$ V, yet this was 0.12 V lower than the measured E_7 of 0.97 V for unsubstituted phenol. The reduction potential E_7 of methoxyphenoxyl radicals satisfies the Hammett correlation using Brown σ^+ substituent constants, as do other monosubstituted phenoxyls if the additivity of σ^+ values is assumed and the state of protonation of the substituents is taken into consideration. The derived $\sigma^+(CH_3O)_m$ value of −0.14, in contrast to reported positive values, indicates the contribution of the methoxy group, even in the meta position, to charge delocalization and resonant stabilization of the phenoxyl radical. The contribution of the ring structure to more negative σ^+ values was observed, as expected. Use of the Hammett correlation is suggested for rapid estimation and accurate calculation of the redox potentials of polysubstituted phenolic antioxidants.

Introduction

Understanding the role and mechanisms of various cellular, physiological, and dietary constituents as inhibitors of deleterious oxidative processes and their putative consequences—inflammation, physiological disorders, and degenerative processes, such as aging, cancer, and cardiovascular diseases—advanced dramatically during the 1980s. An essential part of that progress has been the availability of oxidation potentials under homogeneous (nonelectrode) conditions of ascorbate ($E_7 = 0.28$ V),[3] vitamin E ($E_7 = 0.48$ V),[3] urate ($E_7 = 0.59$ V),[4] serotonin ($E_7 = 0.64$ V),[5] and tyrosine ($E_7 = 0.94$ V),[6] a group of compounds that act as physiological antioxidants in vivo. In many instances, the accuracy of these measurements by pulse radiolysis has been hampered by the lack of appropriate redox standards with oxidation potentials close to that of the antioxidant under investigation and with distinct nonoverlapping absorption of the radical of the redox standard. Furthermore, the predictability of redox potentials based on structural features of potential electron donors is still lacking.

The oxidation potentials and other physicochemical properties (pK_a values, λ_{max}, ϵ, and k values for formation and decay) are presented for six phenolic compounds and their radicals that may satisfy the requirements for redox standards. The main advantages of these compounds are an adjustable range of oxidation potentials created by substituent effects ($E_7 = 0.58$–0.97 V), a broad range of absorption maxima ($\lambda_{max} = 300$–505 nm) with strong absorbancies (4000–7000 $M^{-1}\,cm^{-1}$) of free radical intermediates, and convenient solubilities both in aqueous and polymeric media. Hence, methoxyphenols are suggested as convenient redox standards not only of physiological antioxidants but also of antioxidants in diverse technological materials. The measured E_7 values were used to demonstrate additivity of Brown substituent constants σ^+, which allows development of accurate calculations of one-electron reduction potentials for a number of potential, complex, phenolic antioxidants.

Materials and Methods

Methoxyphenols were purchased from Aldrich[7] or Sigma and were recrystallized 3 times from petrol ether before use. Sesamol was a product of Sigma (99%) and was used as received. Promethazine hydrochloride was obtained from Sigma. Water was purified through a Millipore Milli Q system. All solutions were freshly prepared before use. The pH of the solutions was adjusted by KOH (Merck or Carlo Erba) and $HClO_4$ (Merck) or maintained by phosphate (Merck) and borate (Zorka) buffers. To convert solvated electrons to $^{\bullet}OH$ radicals, the solutions were saturated with N_2O (Tehnogas) that contained less than 2 ppm oxygen.

The Febetron 707 pulse radiolysis at The Boris Kidric Institute is detailed elsewhere.[8] Thiocyanate dosimetry[9] was used for dose determinations, taking $G[(SCN)_2^{\bullet -}] = 6.0$ in N_2O-saturated aqueous solution of 10 mM KSCN and $\epsilon_{480} = 7600$ $M^{-1}\,cm^{-1}$. The doses used corresponded to radical concentrations from 0.6 to 10 μM.

Results

Generation and Characterization of Methoxyphenoxyl Radicals. The methoxyphenoxyl radicals were generated from methoxy-substituted phenols by $Br_2^{\bullet -}$ induced oxidation.[5]

$$Br_2^{\bullet -} + (CH_3O)_nPhOH \rightarrow 2Br^- + (CH_3O)_nPhOH^{\bullet +} \quad (1)$$

The reaction rate constants, k, of reaction 1 were determined from the pseudo-first-order decay of the bromide radical anion at 355 nm.[10] The reactivities of $Br_2^{\bullet -}$ with methoxyphenols and the properties of resulting methoxyphenoxyl radicals are summarized in Table I.

The decay and spectral properties of the methoxyphenoxyl radicals (Table I) were unaffected by variation of the pH from 3 to 14 or the ionic strength of the solution from 0.01 to 2 M. Consequently

$$(CH_3O)_nPhOH^{\bullet +} + H_2O \rightleftharpoons (CH_3O)_nPhO^{\bullet} + H_3O^+ \quad (2)$$

$$pK_a < 2$$

Similar acid–base properties, $pK_a < 0$, were reported[12] for a series of monosubstituted phenoxyl radical cations.

One-Electron Redox Potentials of Methoxyphenols. In general, one-electron redox potentials are derived from the following equilibrium:

$$A^{\bullet} + D^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^- + D^{\bullet} \quad (3)$$

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TABLE I: Reactivities of Methoxyphenols (ArOH) with $Br_2^{\bullet-}$, and Spectral Properties and Decay Rates (2*k*) of Corresponding Phenoxyl Radicals (ArO•) Determined by Pulse Radiolysis in Aqueous Solutions at 20 °C

		ArO•		
parent methoxyphenol, ArOH	$k(Br_2^{\bullet-} + ArOH)$,[a] $M^{-1}\ s^{-1}$	λ_{max},[b] nm	ϵ_{max},[a] $M^{-1}\ cm^{-1}$	$2k$,[a] $M^{-1}\ s^{-1}$
4-methoxyphenol	8.8×10^7	420	7000[c]	1×10^9[c]
2,6-dimethoxyphenol	4.6×10^8	<300	*d*	*d*
3,4-dimethoxyphenol	6.3×10^8	430	6000	1.3×10^9
sesamol	2.6×10^8	435	5000	5.0×10^8
3,5-dimethoxyphenol	6.1×10^8	505	4000	1.3×10^9
3,4,5-trimethoxyphenol	5.6×10^8	495	6000	1.25×10^9

[a] Estimated to be accurate to ±10%. [b] The position of the maximum ±2 nm. [c] From ref 11. [d] Not determined.

TABLE II: Kinetics (*k*), Equilibrium Constant (*K*), and Redox Potential Difference (Δ*E*) for Electron-Transfer Reactions of Methoxyphenols (A^-), Electron Donors (D^-), and Their Corresponding Radicals in Aqueous Solutions at 20 °C

$$A^\bullet + D^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^- + D^\bullet$$

acceptor, $A^\bullet$	donor, D^-	pH	k_f,[a] $M^{-1}\ s^{-1}$	k_r,[a] $M^{-1}\ s^{-1}$	K_{kin}[b]	K_{abs},[b]	ΔE,[c] V
3,4-dimethoxyphenol	$Fe(CN)_6^{4-}$	13.5	6.5×10^5	2.7×10^4	24[d]	*g*	0.08[d]
	N,N'-DMAMF	7.0	2.9×10^7	8.7×10^5	34	48	0.095
3,5-dimethoxyphenol	FDC	7.0	1.1×10^9	6×10^5	1830	1700	0.19
	FDC	8.0	7.0×10^8	2×10^6	350	368	0.15
	4-MeOphenol	13.5	8.0×10^8	1.8×10^6	444	456	0.16
sesamol	$Fe(CN)_6^{4-}$	13.5	8.2×10^5	2.4×10^5	3[d]	3[d]	0.03
	TMPD	13.5	1.5×10^9	*e*			
2,6-dimethoxyphenol	FDC	7.0	*g*	6.5×10^6			
	TMPD	13.5	1.2×10^9	*g*	*g*	380	0.15
3,4,5-trimethoxyphenol	promethazine	3.0[f]	1×10^6	2.1×10^7	0.05	0.05	−0.08

[a] Estimated to be accurate to ±10% for the reactions in the favorable direction and to ±20% for the reverse reactions. [b] Equilibrium constants derived from kinetics, K_{kin}, and from equilibrium absorbencies of radicals, K_{abs}. [c] Redox potential difference between the acceptor and the donor calculated from the mean equilibrium constant, $K = (K_{abs} + K_{kin})/2$, using the Nernst equation, $\Delta E = 0.059 \log K$. [d] The ionic strength was $I = 0.5$ M. The change in the reverse reaction due to the increased ionic strength was found to be <20%. The redox potential of the $Fe^{3+}/Fe^{2+}(CN)_6$ is $E = 0.455$ V at $I = 0.5$ M.[14] [e] Irreversible. [f] $Cl_3COO^\bullet$ was used as a primary oxidant (see ref 5). [g] Not determined.

where $A^\bullet$ is a free radical of compound A^- (or AH) and D^- is a convenient electron donor with a well-established redox potential. The redox potential may be expressed either as the reduction potential of the radical $E(A^\bullet/A^-)$, i.e., $E(A^\bullet/AH)$, depending on pH, or as the oxidation potential of the compound. When applied to the same redox couple, reduction and oxidation potentials are by convention numerically equal.

The equilibrium constant, *K*, for reaction 3 is given by

$$K = k_f/k_r = [A^-][D^\bullet]/[A^\bullet][D^-] \qquad (4)$$

Hence, the *K* value can be derived either as K_{kin} from kinetic data or as K_{abs} from the concentrations of the reactants at the equilibrium, i.e., absorptions of the intermediates.

The redox potentials of methoxyphenols were determined for the half-cell reaction of methoxyphenoxyl/methoxyphenol redox couples:

$$(CH_3O)_nPhO^\bullet + e^- \rightleftharpoons (CH_3O)_nPhO^- \qquad (5)$$

The electron-transfer reactions of methoxyphenols and the corresponding radicals were studied at pH 13.5, where simple, reversible, and faster electron-transfer reactions occurred due to deprotonation of methoxyphenols (see Table IV for pK_a values):

$$(CH_3O)_nPhO^\bullet + D^- \rightleftharpoons (CH_3O)_nPhO^- + D^\bullet \qquad (6)$$

The reduction potential of the radical (i.e., one-electron oxidation potential of the parent phenol) was calculated from the Nernst equation. At 20 °C

$$\Delta E = 0.059 \log K \qquad (7)$$

where the equilibrium constant *K* was taken as an average value of K_{kin} and K_{abs} (see Table II). At pH 7 and 3, a proton is also transferred, in addition to an electron (reaction 8). Primary

$$(CH_3O)_nPhO^- + H^+ \rightleftharpoons (CH_3O)_nPhOH \qquad (8)$$

inorganic one-electron redox standards, $Fe^{3+}/Fe^{2+}(CN)_6$ with $E = 0.36$ V,[13] ferrocenedicarboxylate with $E_7 = 0.66$ V,[14] and [(*N,N'*-dimethylamino)methyl]ferrocene with $E_7 = 0.59$ V,[14] were used because of their accurate redox potentials. The organic one-electron redox standards, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) with $E = 0.27$ V,[3] 4-methoxyphenol with $E_{13.5} = 0.54$ V,[5] and promethazine with $E_3 = 0.98$ V,[5] were used when the reactions of methoxyphenoxyl radicals with inorganic redox standards could not be determined. The results are summarized in Table II.

TABLE III: One-Electron Oxidation Potentials of Methoxyphenols vs NHE in Aqueous Solutions at 20 °C

methoxyphenol	E_0[a]	E_7[b]	$E_{13.5}$[b]
phenol	1.38[c]	0.97[c]	0.79[c]
4-methoxyphenol	1.13[d]	0.73[d]	0.54[d]
3,5-dimethoxyphenol	1.26	0.85	0.71
3,4,5-trimethoxyphenol	1.08	0.66	0.55
3,4-dimethoxyphenol	1.08	0.67	0.50
sesamol	1.02	0.62	0.45
2,6-dimethoxyphenol	0.99	0.58	0.42

[a] Calculated from formula 9 in the text, in volts. [b] In volts, estimated to be accurate to ±0.02 V. [c] From ref 6. [d] From ref 5.

The rates of oxidation of ferrocyanide at pH 13.5 by 3,4-dimethoxyphenoxyl and sesamol radicals were low, $k \sim 10^5$–10^6 $M^{-1}\ s^{-1}$, which could result in a nonequilibrium electron transfer due to rapid radical decay (see Table I). This was circumvented by high concentrations of solutes (1–10 mM $Fe(CN)_6^{4-}$ and ~40 mM dimethoxyphenol) and a low dose rate (1 Gy/pulse), at which the concentration of radicals was only 0.6 μM. The low rates of electron transfer associated with the $Fe^{3+}/Fe^{2+}(CN)_6$ couple are the most serious drawback to the use of this redox standard. The

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TABLE IV: Acid–Base Properties of Phenols (pK_a) and Corresponding Phenoxyl Radicals (pK_r), Reduction Potentials at pH 7 (E_7) from Refs 5 and 6, Table III, and Substituent Constants (σ^+)

				pH 7		pH 0	
point	substituent	pK_a[a]	pK_r[b]	E_7, V	σ^{+}[c]	E_0, V	σ^{+}[c]
1	H	1.0	−2	0.97	0	1.38	0
2	4-O⁻/4-OH	9.91;12.04	−0.8;4.1[d]	0.46[d]	−1.6	1.04	−0.92[b]
3	4-$(CH_3)_3N$	8.0	<0[e]	0.36	−1.70	0.77	−1.70
4	4-NH_2	8.5;10.3	unknown	0.41	−1.31		
5	4-OCH_3	10.2	<0[e]	0.73	−0.78	1.14	−0.78
6	4-CH_3	10.19	−1.9	0.87	−0.31	1.28	−0.31
7	4-F	9.95	<0[e]	0.93	−0.08	1.34	−0.08
8	4-Cl	9.43	<0[e]	0.94	0.11	1.35	0.11
9	4-Br	9.34	<0[e]	0.96	0.15	1.37	0.15
10	4-I	9.31	<0[e]	0.09	0.13	1.37	0.13
11	4-CO_2^-	9.39;4.58	unknown	1.04	0.0		
12	4-$COCH_3$	8.05	<0[e]	1.06	0.50	1.47	0.50
13	4-CN	7.95	<0[e]	1.17	0.66	1.58	0.66
14	4-NO_2	7.14	<0[e]	1.23	0.79	1.63	0.79
15	3-O⁻/3-OH	9.8;11.3[d]	−1.5;7[d]	0.81[d]	−0.47	1.24	−0.04[h]
16	3,5-$(CH_3O)_2$	9.345	<0	0.85	−0.28[f]	1.26	−0.28
17	3,4-$(CH_3O)_2$	9.80	<0	0.67	−0.92[f]	1.08	−0.92
18	3,4,5-$(CH_3O)_3$	8.95	<0	0.66	−1.06[f]	1.07	−1.06
19	2,6-$(CH_3O)_2$	9.63	<0	0.58	−1.34[f]	0.99	−1.34
20	(sesamol)	9.70	<0	0.62	−1.06[g]	1.03	−1.06
21	(α-tocopherol)	11.9[d]	<0[e]	0.48[d]	−1.52[g]	0.89	−1.52

[a] From ref 16. [b] From ref 12 and this study. [c] From ref 17. [d] From ref 3 and references therein. [e] Derived from similarities with other phenoxyls. [f] Calculated as $\sum\sigma^+$. See Discussion for details. [g] Calculated from eq 10 (see text). [h] OH value at pH 0.

reason for the low rates is very likely the high reorganization energy of the Fe–cyanide complex.[15]

This was not the case in the reactions of ferrocene derivatives, where the reaction rate constants were higher, 10^7–10^8 M^{-1} s^{-1} (see Table II). Unfortunately, the oxidized ferrocenes exhibit weak absorption spectra in the visible region, i.e., $\lambda_{max} \sim 600$ nm and $\epsilon_{max} = \sim 600$ M^{-1} cm^{-1},[14] so the parameters of the electron-transfer reactions could not be accurately determined from their spectra. Consequently, the use of ferrocenes as redox standards is severely limited, and ferrocenes can be used only for those reactions which generate strongly absorbing radicals.

The redox potentials at a different pH were calculated from

$$E_i = E_0 + 0.059 \log (K_a + 10^{-i}) \qquad (9)$$

where E_i and E_0 are the oxidation potentials at pH i and 0, respectively, and K_a is the acid–base dissociation constant of methoxyphenol, with values expressed as pK_a's in Table IV. The results are summarized in Table III. The standard potentials, E_0, were obtained as the arithmetic mean of the values calculated from the potentials measured at different pH's. These standard potentials were then used to evaluate the pH dependence of the oxidation potentials.

Discussion

Accurate measurement of redox potentials of antioxidants is a tedious and often difficult undertaking for many reasons, including slow kinetics, lack of convenient absorption bands of intermediates, instrumental limitations, and lack of simple free-radical-generating mechanisms. Hence, the predictability of redox potentials based on the electronic structure of organic compounds in general, or antioxidants in particular, becomes highly desirable. In addition, predictability would greatly assist in designing a suitable antioxidant with desirable properties. Such predictability may be achieved through the Hammett correlation.[17]

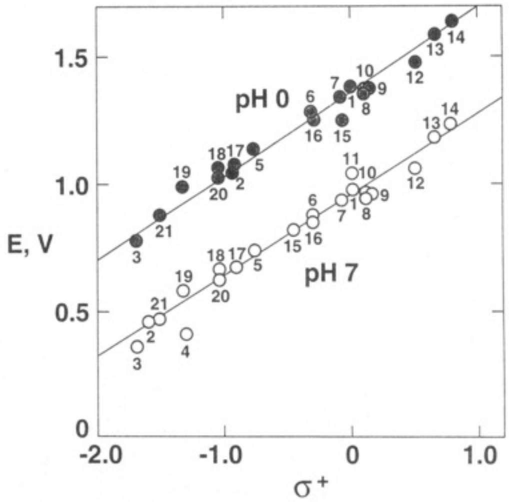

Figure 1. The Hammett plot of the reduction potentials of various phenoxyl radicals in aqueous solutions at 20 °C vs σ^+. Open symbols correspond to the data at pH 7 (the line is described by $E_7 = 0.95 + 0.31\sigma^+$, correlation coefficient = 0.987), whereas filled symbols represent the standard potentials (pH 0), calculated from the measured E values and relevant dissociation constants (the line is described by $E_0 = 1.34 + 0.32\sigma^+$, correlation coefficient = 0.985).

Hammett Correlation for Redox Potentials. As recently shown,[6] there is a linear correlation between log K' of the Nernst equation for para-substituted phenoxyl radicals and Brown[18] substituent constants σ^+. Very recently a good correlation was also observed between σ^+ constants and oxidation potentials of phenoxide ions measured by cyclic voltammetry in DMSO and acetonitrile.[19]

A linear relationship was derived between the one-electron reduction potentials of para-substituted phenoxyl radicals at pH 7 (E_7) and pH 0 (E_0) and the σ^+ values of substituents (points 1–14 in Table IV and Figure 1). The relationship at pH 7 can be described by the following expression (best fit, excluding point 4, correlation coefficient 0.987):

$$E_7 = 0.95 + 0.31\sigma^+ \qquad (10)$$

Since

$$E = E(\text{PhO}^\bullet/\text{PhOH}) + \rho\sigma^+ \qquad (11)$$

it follows that $E_7(\text{PhO}^\bullet/\text{PhOH}) = 0.95$ V and $\rho = 0.31$. The derived value of 0.95 V for the reduction potential of the phenoxyl

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radical (equivalent to the one-electron oxidation potential of phenol) is only slightly lower than the experimentally derived value of 0.97 V (Table IV). Similarly, the best fit (correlation coefficient 0.985) for calculated redox potentials at pH 0 gives

$$E_0 = 1.34 + 0.32\sigma^+ \qquad (12)$$

It is interesting to note similar ρ values for pH 0 and 7.

The correlation of E_7 and E_0 with σ^+ (Figure 1) clearly indicates the role of resonance and partial distribution of the charge.[6,19–21] Better electron-donating substituents (more negative σ^+ values) reduce the redox potential of the phenols and increase the rate and efficacy of peroxy radical inactivation by antioxidants.[18,19] Electron-withdrawing substituents (higher positive σ^+ values), on the other hand, increase the redox potential of phenols, disqualifying these particular phenols as antioxidants, since $E_7(\mathrm{ROO^\bullet/ROOH}) \sim 0.9$ V.[22]

State of Protonation. Free radicals usually have lower pK_a values than parent compounds.[23] For example, the para OH substituent in the phenoxyl radical at pH 7 is in the O^- state because pK_r = 4.1 (Table IV). Hence, $\sigma^+(O^-)_p = -1.6$ was used in Figure 1 (point 2) rather than $\sigma^+(OH)_p = -0.92$ at pH 0. The excellent fit of point 2 demonstrates the need to take into consideration the acid–base properties of phenoxyl radical substituents when selecting appropriate σ^+ values and the role of charge distribution not only in the phenols but also in their corresponding radicals.

The reason for the large deviation of para-amino-substituted phenoxyl radical (point 4 in Figure 1) from the line is not obvious. As in the case of the para OH substituents, the amino group may be in the deprotonated form, NH^-. This would increase the resonant character (delocalization of charge) and would make the σ^+ more negative, bringing it closer to the line. Unfortunately, the $\sigma^+(NH^-)_p$ value is not available to verify this prediction. Further work is required to resolve this issue and provide a new approach for determination of the state of protonation of polysubstituted phenoxyl radicals.

Additivity of σ^+ Values. The available σ^+ values for the substituent CH_3O in the meta position are 0.046[18] and 0.09.[17,18] Both values are positive, and, consequently, one would expect that phenoxyls with meta substituents should have an E_7 greater than 0.95 (or 0.97)[6] V, as is found for other substituents with positive σ^+ values (Table IV). This was not observed for the 3,5-$(CH_3O)_2$-substituted phenoxyl, for which a decrease in E_7, outside experimental error, was observed (E_7 = 0.85 V). From eq 10, 3,5-$(CH_3O)_2$, and 3,4-$(CH_3O)_2$, an average value is derived for $\sigma^+(CH_3O)_m = -0.14 \pm 0.02$. The very good fit of points 16–18 fully justifies the assignment of negative values for $\sigma^+{}_m$, which indicate contributions of meta substituents to resonant stabilization of the phenoxyl and the additivity of σ^+ values for multiple substituents.

Taking the value from the literature[17] for $\sigma^+(2\text{-}CH_3O) = -0.67$ and assuming additivity of σ values, we calculate $\sigma^+(2,6\text{-}(CH_3O)_2) = -1.34$. The good fit of point 19 confirms the additivity rule, as described for other polymethoxyphenoxyls.

Cyclization of Substituents. In addition to having multiple substituents, certain antioxidants, such as vitamin E and sesamol, have another ring associated with the benzene nucleus. In vitamin E, a six-membered ring has oxygen in the position para to the OH group. The fused heterocyclic system is referred to as a chroman. In sesamol, a five-membered ring is fused to phenol, with two oxygens, one each in the para and meta position. Assuming similar σ^+ values for CH_3O- and $-CH_2O-$ groups, as well as for CH_3- and $-CH_2-$, we calculate for α-tocopherol and sesamol $\sum\sigma^+ = -1.46$ and -0.92, respectively, using[17] $\sigma^+(CH_3)_o = -0.27$ and $\sigma^+(CH_3)_m = -0.07$. Slightly lower σ^+ values, calculated from eq 10 and E_7 values in Table IV, are in agreement with the observation that a fused heterocyclic ring structure contributes to the resonant stability of these complex phenoxyl radicals.[20]

Conclusions

The direct correlation of redox potentials of a number of antioxidants with Brown substituent constants, σ^+, in aqueous solutions, allows calculation of E_7 for numerous biologically and nutritionally relevant physiological and plant phenolic antioxidants. Certain σ^+ values, however, may still be missing for calculating E_7 of complex antioxidants. They may be derived readily from pulse radiolytic measurements using simpler model compounds.

The additivity of σ^+ values in complex antioxidants now allows fine tuning of redox potentials to fit the required properties in media as diverse as materials, devices, foods, and biomedical systems.

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Registry No. FDC, 1293-87-4; *N,N*-DMAMF, 1271-86-9; TMPD, 100-22-1; Fe, 7439-89-6; $Fe(CN)_6{}^{4-}$, 13408-63-4; $Br_2{}^{\bullet-}$, 12595-70-9; 4-methoxyphenol, 150-76-5; promethazine, 60-87-7; 2,6-dimethylphenol, 91-10-1; 3,4-dimethylphenol, 2033-89-8; sesamol, 533-31-3; 3,5-dimethoxyphenol, 500-99-2; 3,4,5-trimethoxyphenol, 642-71-7; 4-methoxyphenoxyl, 3174-48-9; 2,6-dimethoxyphenoxyl, 15773-12-3; 3,4-dimethoxyphenoxyl, 115061-01-3; sesamoxyl, 62266-17-5; 3,5-dimethoxyphenoxyl, 58864-28-1; 3,4,5-trimethoxyphenoxyl, 137626-76-7.

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