photocatalytic decomposition of water in the vapor as well as liquid phase about 100 times higher than that of $SrTiO_3$ alone. In this reaction the initial step is the absorption of a photon in the semiconductor, $SrTiO_3$, and production of an electron (e^-) in its conduction band and a hole (h^+) in its valence band. According to the electrochemical results, on a n-type semiconductor such as $SrTiO_3$ (E_{gb} = 3.2 eV), a hole can migrate easily to the surface and an electron to the bulk, because of the band bending near the surface. Accordingly, it is necessary to have some short circuit for the electron to migrate with ease to the surface of $SrTiO_3$. Consequently, it is possible that the conduction band electron reacts with H^+ through NiO and H_2 is produced. The pretreatments of reduction and reoxidation may make the contact between NiO and $SrTiO_3$ better for the electron transfer. The effect of supported NiO was detected clearly even when the amount of NiO was small (<1 wt %), as shown in Figure 4, which indicates that highly dispersed NiO is an effective component, and bulky NiO is not necessary to get activity (0.6 wt % of NiO is required to form a monolayer of NiO on the surface of $SrTiO_3$, calculated from the results of BET measurements).

Adsorbed water was necessary to decompose water molecules to H_2 and O_2 and surface hydroxyl groups alone; i.e., in the absence of adsorbed water, we could not produce any H_2 or O_2, as shown in Figure 6. On the other hand, direct oxidation of H_2O molecules to H_2O^+ by a hole in the valence band of $SrTiO_3$ is energetically unfavorable.[17] It seems reasonable to suppose a feasible reaction between a hole (h^+) and OH^-(a), which is produced by a rapid equilibrium with H_2O(a) in eq 1. The OH^-(a) species in

$$H_2O(a) \rightleftarrows H^+(a) + OH(a) \quad (1)$$

eq 1 should be distinguished from that in stable Ti–OH which remains even after the pretreatments and exhibits no activity for the photodecomposition. Damme et al.[12] also suggested that the formation of the Ti–OH bond on the surface is a very slow step.

In the lower H_2O pressure region (9×10^2 Pa), only H_2, not O_2, evolved; that is, the reaction was not catalytic, as shown in Figure 5. This suggests that much H_2O(a) is necessary for the evolution of O_2. When the H_2O pressure was increased from 4×10^2 to 2.7×10^3 Pa, H_2 and O_2 began to evolve in stoichiometric amounts. The oxidized species which could not evolve to the gas phase as O_2 under 4×10^2 Pa of H_2O seems to be trapped irreversibly in the surface.

On the basis of the results obtained so far, the following mechanism is tentatively proposed for the photodecomposition of water vapor on NiO–$SrTiO_3$:

$$H_2O(g) \rightleftarrows H_2O(a) \rightleftarrows H^+(a) + OH^-(a) \quad (1')$$

$$SrTiO_3 + h\nu \rightarrow h^+ + e^- \quad (2)$$

On NiO

$$2H^+(a) + 2e^- \rightarrow 2H\cdot(a) \rightarrow H_2(a) \rightarrow H_2(g) \quad (3)$$

On $SrTiO_3$

$$h^+ + OH^- \rightarrow OH\cdot \quad (4)$$

$$4OH\cdot \rightarrow \ldots \rightarrow O_2(a) + 2H_2O(a) \rightarrow O_2(g) \quad (5)$$

The rate of photodecomposition of pure liquid water was about 3 times faster than that of water vapor. Although this seems attributable to the difference in the amount of H_2O(a), extrapolating the results in Figure 5, a detailed study will be reported in a later publication.

(17) The ionization potential of H_2O = 12.6 eV; the hydration energy of H_2O^+ = ca. 3 eV; the energy of h^+ in the valence band of $SrTiO_3$ = 7.2 eV (vs. vacuum level); 12.6 eV > 3 + 7.2 eV. Another possibility for the reaction between H_2O(a) and h^+ may be $H_2O(a) + h^+ \rightarrow H^+(a) + OH\cdot(a)$.

One-Electron Redox Potentials of Phenols. Hydroxy- and Aminophenols and Related Compounds of Biological Interest[1]

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The rate constants for reversible electron transfer between a series of substituted phenolate ions and anilines and various substituted phenoxyl or anilino radicals in aqueous solution were measured by observing the formation or depletion of the radicals involved. Nonequilibrium concentrations of the radicals were produced in the presence of the corresponding phenols or anilines by using the pulse radiolysis technique. The relaxation of the system to equilibrium was monitored by optical detection methods. From the equilibrium constants for one-electron transfer, the one-electron redox potentials (E^2) for 38 phenolic or anilino type compounds were determined, many of which are natural products. The redox potentials are strongly influenced by electron-donating or -withdrawing substituents at the aromatic system.

Introduction

The oxidation of phenols is of great interest because of their involvement in important biological and industrial processes. Phenolic compounds are members of the groups of hormones, vitamins, and food antioxidants. The latter group consists almost exclusively of phenols, many of which are natural products.[2-4] The mechanism of their

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2312 from the Notre Dame Radiation Laboratory.

(2) Howard, J. A. *Adv. Free-Radical Chem.* **1972**, *4*, 49. Ingold, K. U. *Adv. Chem. Ser.* **1968**, *No. 75*, 296. Mahoney, L. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 547.

0022-3654/82/2086-3661$01.25/0

action as antioxidants seems to involve the ability of phenols to scavenge radicals by an H-atom or electron transfer process by which the phenol is converted into a phenoxyl radical.[2] Obviously, the ease of oxidation of the phenol will be of importance for its effectiveness as an antioxidant.

In antioxidant action, synergistic effects are often observed, which in many cases seem to involve the regeneration of one antioxidant by a second one via H or electron transfer between the two. Again, a knowledge of the relative position of the synergists with respect to the ease of oxidation is important for understanding the mechanism of synergistic action. Furthermore, phenols are the building blocks of numerous natural products, including many alkaloids, and the biosynthesis of these compounds (by oxidative coupling) seems to proceed via phenoxyl radicals.[5]

For these and other reasons, attempts have previously been made to determine the thermodynamic one-electron redox potentials of phenols.[6-10] However, the short lifetimes of most of the phenoxyl radicals produced by oxidation prevented the establishment of equilibrium between phenols and phenoxyl radicals. Nevertheless, it was possible to measure relative redox potentials[7,8] that proved to be quite useful for explaining reactions of phenols in redox systems.[2,5,10-12]

We have previously shown[13] that the fast-response pulse radiolysis method can be used to produce nonequilibrium concentrations of phenoxyl radicals in the presence of the corresponding phenols and that the relaxation of the system to equilibrium can be kinetically followed by using optical detection methods. It is thus possible to determine "absolute", i.e., thermodynamic, redox potentials. We now report redox potential data obtained by this method for various substituted phenols and compounds of biological interest.

Method

The method of production of phenoxyl radicals and observation of their optical absorptions and kinetic behavior by pulse radiolysis has been described.[13] The same procedure was followed in this study. The substrates (purest grade commercially available, usually purchased from Aldrich, Eastman, or Fluka) were dissolved in N_2O-saturated water containing 0.9 M ethylene glycol and then KOH was added with continuous N_2O purging to make 0.5 M. This procedure was found to prevent the air oxidation of phenoxide ions at high pH. The solution was then passed through the optical quartz cell and irradiated with 8-MeV electrons from a linear accelerator. The pulses were of 5–10-ns duration and delivered energy to the solution to produce 1–2 μM of radicals.

The radiolysis of water produces e_{aq}^-, OH, and H. The N_2O converts e_{aq}^- into OH, which, together with H, react with the ethylene glycol rather than with the aromatic compounds present at lower concentrations. The $HOCH_2\dot{C}HOH$ radical produced undergoes rapid elimination of water at high pH to yield $\dot{C}H_2CHO$, which in turn oxidizes the phenols and anilines.[14] The experiments were carried out at high pH not only in order to achieve a very rapid formation of $\dot{C}H_2CHO$ but also because $\dot{C}H_2CHO$ oxidizes phenoxide ions much more rapidly than phenols.[13,14]

TABLE I: Rate Constants for Reaction of $\dot{C}H_2CHO$

no.[a]	substrate	k,[b] M^{-1} s^{-1}
	o-phenylenediamine	7.7×10^7
		7.3×10^7 [c]
	p-phenylenediamine	4.6×10^8
		4.0×10^8 [c]
	N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD)	2.1×10^9
		2.0×10^9 [c]
	p-(*N,N*-dimethylamino)phenol (DMAP)	2.2×10^9
12	5-hydroxyindole	1.3×10^9
16	5-hydroxytryptophan	1.3×10^9
1	4-methoxyphenol	8.3×10^8
		9.8×10^8 [c]
	catechol	7.4×10^8 [c]
2	resorcinol	1.3×10^9
		1.6×10^9 [c]
	hydroquinone	2.2×10^9 [c]
3	norepinephrine	1.5×10^9
4	DL-β-3,4-dihydroxyphenylalanine (DOPA)	1.4×10^9
5	2,5-dihydroxyphenylacetate	1.7×10^9
8	3,4-dihydroxycinnamate (caffeic acid)	2.6×10^9
7	5-hydroxydopamine	1.8×10^9
9	6-hydroxydopamine	1.8×10^9
6	3,4,5-trihydroxybenzoate (gallate)	1.4×10^9
10	7-hydroxycoumarin (unbelliferone)	1.3×10^9
11	6,7-dihydroxycoumarin (esculetin)	2×10^9
13	ellagic acid	2.4×10^9
14	quinalizarin (1,2,5,8-tetrahydroxyanthraquinone)	2.4×10^9
17	quercetin (3,3',4',5,7-pentahydroxyflavone)	3.1×10^9
18	rutin	1.5×10^9
19	catechin	1.8×10^9
	6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylate (HTCC)	1.8×10^9
15	2,4,5-trihydroxypyrimidine (isobarbiturate)	1.6×10^9

[a] This number identifies the compounds in Figure 1. [b] Determined at pH 13.5 except where noted. [c] Determined at pH 11.5, ref 14.

The rate constants for the one-electron oxidation of various substrates by $\dot{C}H_2CHO$ (reactions 1 and 2), determined by monitoring the buildup of absorption of the resultant aromatic radicals, are summarized in Table I. Most of the compounds studied are derivatives of hydroxy- or aminophenols and are oxidized by $\dot{C}H_2CHO$ practically with diffusion-controlled rates. Only the phenylenediamines react significantly more slowly, and among these the ortho is slower than the para.

$$XC_6H_4O^- + \dot{C}H_2CHO + H^+ \rightarrow XC_6H_4\dot{O} + CH_3CHO \quad (1)$$

$$XC_6H_4NH_2 + \dot{C}H_2CHO \rightarrow XC_6H_4\dot{N}H + CH_3CHO \quad (2)$$

The radicals produced by oxidation with $\dot{C}H_2CHO$ exhibit absorption spectra with λ_{max} and ϵ strongly dependent upon their structure. Spectra of various substituted phenoxyl radicals have been reported previously (e.g., ref 15–21). Specific cases studied in the present work are

(3) Scott, G. "Atmospheric Oxidation and Antioxidants"; Elsevier: Amsterdam, 1965; p 115.
(4) Reich, L.; Stivala, S. S. "Autoxidation of Hydrocarbons and Polyolefins"; Marcel Dekker: New York, 1969.
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(13) Steenken, S.; Neta, P. *J. Phys. Chem.* **1979**, *83*, 1134.
(14) Steenken, S. *J. Phys. Chem.* **1979**, *83*, 595.
(15) Adams, G. E.; Michael, B. D. *Trans. Faraday Soc.* **1967**, *63*, 1171.
(16) Land, E. J.; Ebert, M. *Trans. Faraday Soc.* **1967**, *63*, 1181.
(17) Bors, W.; Saran, M.; Michel, C.; Lengfelder, E.; Fuchs, C.; Spöttl, R. *Int. J. Radiat. Biol.* **1975**, *28*, 353.

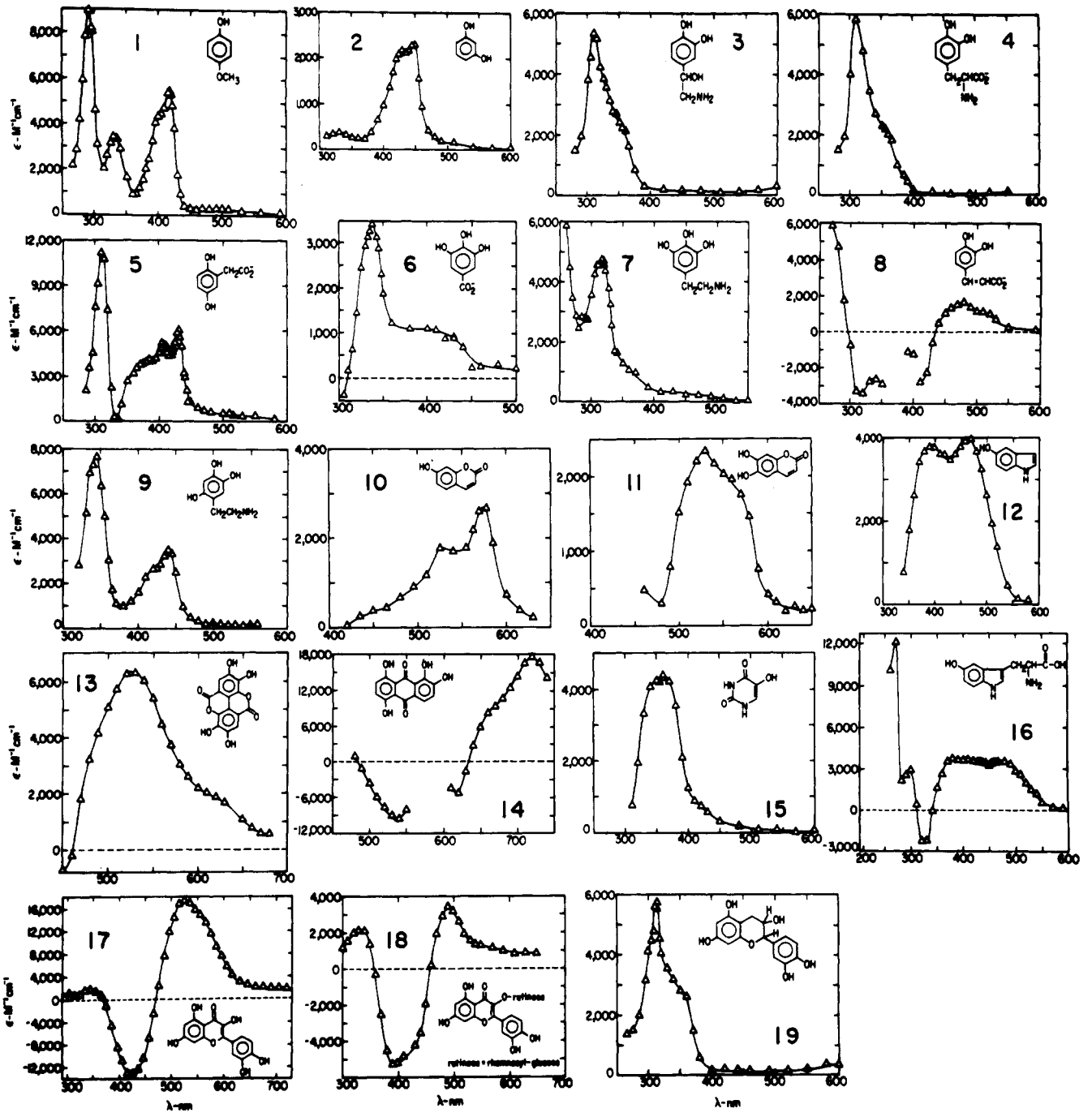

Figure 1. Transient differential absorption spectra observed upon one-electron oxidation of various phenols. Solutions contained 10^{-4}–10^{-2} M of the substrate, 0.9 M ethylene glycol, and 0.5 M KOH and were saturated with N_2O. The spectra were monitored a few microseconds after the pulse, as soon as the reaction of the substrate with $\dot{C}H_2CHO$ was complete. Extinction coefficients were determined by using thiocyanate dosimetry and assuming $G = 6$ and ϵ for $(SCN)_2^-$ at 480 nm 7600 M^{-1} cm^{-1}. The numbers correspond to those in Table I.

shown in Figure 1. The knowledge of these spectra is important for considerations concerning the possible observation of electron transfer reactions between two systems

$$XC_6H_4\dot{O} + YC_6H_4O^- \rightleftarrows XC_6H_4O^- + YC_6H_4\dot{O} \quad (3)$$

In general, it is found that *o*-hydroxy-, *o*-amino- or *o*-alkoxyphenoxyl radicals absorb mainly in the 300–350-nm region while the meta and para analogues absorb in the 400–500-nm region. It is, therefore, usually convenient to study the ortho vs. one of the other isomers. However, in more complex molecules each set has to be considered on the basis of the detailed absorption spectra. When the spectra are sufficiently different, it is possible by optical methods to observe reaction 3. If this reaction is experimentally observable and if equilibrium is achieved before the radicals decay by other processes, it is then possible to determine the equilibrium constant and consequently the redox potential, as described previously.[13,22]

Electron Transfer Rates and Equilibria

The determination of the electron transfer rate constants k_3 and k_{-3} and of the equilibrium constant K from the absorbances at equilibrium is demonstrated by the system

(18) Schuler, R. H.; Buzzard, G. K. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 563.
(19) Bansal, K. M.; Fessenden, R. W. *Radiat. Res.* **1976**, *67*, 1.
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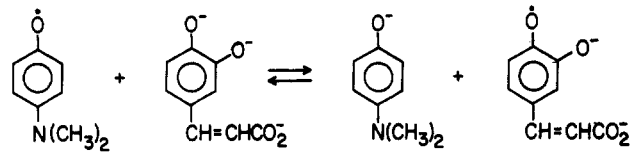
(21) Richter, H. W. *J. Phys. Chem.* **1979**, *83*, 1123.
(22) Meisel, D.; Neta, P. *J. Am. Chem. Soc.* **1975**, *97*, 5198.

TABLE II: Determination of Equilibrium Constant for



(DMAP)• DHC DMAP (DHC)•

[DMAP], mM	[DHC], mM	rel absorb at 490 nm at equilibrium	k_{obsd}, s^{-1}	K^a
2.5	0	8930		
0	0.60	1680		
2.6	0.60	2490	9.9×10^4	35
2.6	0.09	4730	2.4×10^4	37
2.6	0.35	3100	6.4×10^4	30
2.4	0.25	3210	5.1×10^4	36
2.4	0.72	2400	1.2×10^5	30
				av = 34 ± 4

from Figure 2, $k_3/k_{-3} = 30$
$\Delta E = 90$ mV

[a] $K = [DMAP][DHC\cdot]/\{[DHC][DMAP\cdot]\}$.

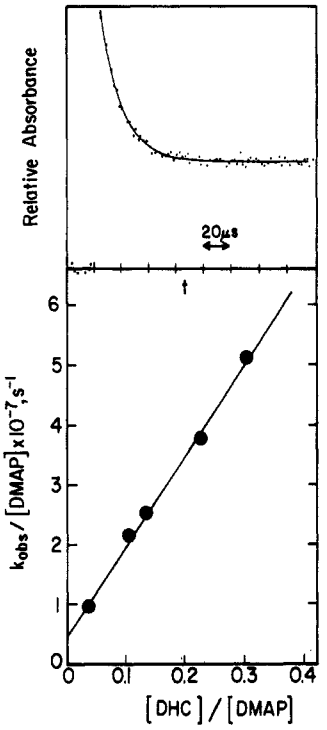


Figure 2. Electron transfer and equilibrium between *p*-dimethylaminophenol (DMAP) and 3,4-dihydroxycinnamic acid (DHC). Top: Experimental points and calculated trace showing change in absorption at 490 nm upon electron transfer from DHC to (DMAP)• to reach equilibrium. Bottom: A plot of the dependence of the rate constant k_{obsd} on the concentrations of substrates. The straight line has a slope of k_3 and an intercept of k_{-3}.

p-(*N*,*N*-dimethylamino)phenol (DMAP) vs. 3,4-dihydroxycinnamate (DHC) in Table II and Figure 2. The absorbances of each of the radicals determined separately and the absorbance at equilibrium allow the determination of the ratio of radical concentrations at equilibrium. The constant K is then calculated from this ratio and the concentrations of the parent compounds in solution. Table II shows that the value of K is indeed constant, within experimental error, over a range of concentrations. Figure 2 (top) shows an example of a kinetic trace which clearly

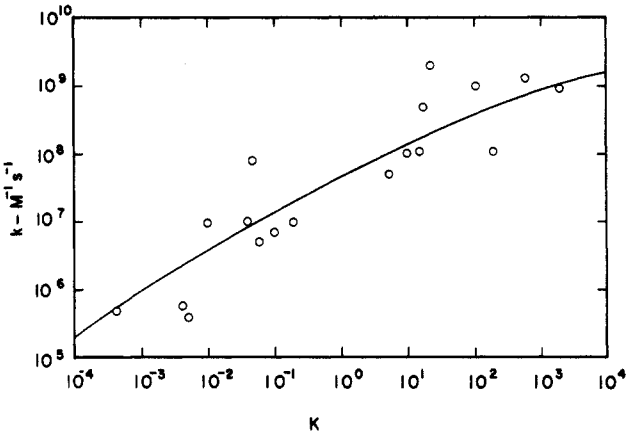


Figure 3. Dependence of rates of electron transfer (k) on the equilibrium constants (K). The data are given in Table III and ref 13. The curve was calculated from the Marcus relation (see text). Only reactions where one of the reactants and one of the products are uncharged are included in this figure.

indicates the achievement of equilibrium and which allows determination of k_{obsd}. Figure 2 (bottom) shows a plot of $k_{obsd}/[DMAP]$ vs. $[DHC]/[DMAP]$ which has k_3 as the slope and k_{-3} as the intercept.[13,22] The value of the equilibrium constant determined from k_3/k_{-3} is in good agreement with that determined from the absorbances (Table II). The difference in redox potential between the two systems is $\Delta E = 0.059 \log K$.

The results for the various systems studied are summarized in Table III. The table lists the values of k_3 and k_{-3} derived from plots such as that shown in Figure 2. In cases where there are no entries for k_{-3} the plots did not yield reliable values of k_{-3}, either because the electron transfer took place predominantly in one direction or because the equilibrium was distorted as a result of rapid radical–radical reactions. The equilibrium constants K were also calculated from the absorbance (=radical concentrations) at equilibrium. In most cases, the value of K thus obtained was in good agreement with the ratio k_3/k_{-3} and then the redox potential difference ΔE was derived from the average of both values.

The rates of the electron transfer reactions, k_3, are expected to become larger as the values of the equilibrium constant K increase, according to the Marcus relation.[23] In fact, a plot of the data from Table III (and from ref 13) clearly shows that, in general, k increases with K in all groups of chemical systems studied. Figure 3 shows such a plot for reactions in which one of the reactants and one of the products are uncharged. The figure includes many of the results for TMPD and DMAP. The experimental points are in reasonable agreement with the curve calculated[24] from the Marcus relation for such reactions. The rest of the data involves cases where all reactants and products are charged. The data (not shown in the figure) are also in agreement with the Marcus relation. Considering that the points in Figure 3 refer to a wide variety of chemical structures and that the curve is calculated by using only one set of molecular parameters, the agreement between the experimental and calculated values is satisfactory. The experimental points with the highest deviation from the general trend probably indicate that other molecular parameters are important that did not enter the calculation. Discussion of specific cases will not be attempted here.

(23) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966; **1957**, *26*, 867, 872.
(24) Using λ = 18 kcal/mol as suggested for similar systems by: Meisel, D. *Chem. Phys. Lett.* **1975**, *34*, 263.

TABLE III: Electron Transfer Rates and Equilibria

$$Ar^1\dot{O} + Ar^2O^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ar^1O^- + Ar^2\dot{O}$$

$$K = ([Ar^1O^-]/[Ar^2O^-])([Ar^2\dot{O}]/[Ar^1\dot{O}])$$

Ar^1OH (or Ar^1NH_2)	Ar^2OH (or Ar^2NH_2)	λ, nm	k_3, M^{-1} s^{-1}	k_{-3}, M^{-1} s^{-1}	K	ΔE, mV
DMAP	hydroquinone	430, 490	1×10^8	3×10^5	405	151
DMAP	catechol	490	3×10^7	2×10^5	130	131
DMAP	3,4-dihydroxyphenylacetate	490	9×10^7		395	153
DMAP	3,4-dihdyoxyphenylalanine	490	7×10^7		508	160
DMAP	norepinephrine	490	3×10^7	2×10^5	162	130
DMAP	3-hydroxytyramine	490	9×10^7	3×10^5	450	156
DMAP	3,4-dihydroxycinnamate	490	1.5×10^8	5×10^6	34	90
DMAP	catechin	490	1.1×10^7	4.5×10^5	67	95
DMAP	epicatechin	490	3×10^7	4×10^5	138	126
DMAP	esculetin	490	1.4×10^8			
DMAP	5-hydroxydopamine	490	1.2×10^7	9×10^4	175	132
DMAP	6-hydroxydopamine	490	$\sim 5 \times 10^8$		>1000	
resorcinol	DMAP	490	$\sim 7 \times 10^7$	$\sim 2 \times 10^4$	5000	218
5-hydroxytryptophan	DMAP	490	3×10^7	2×10^6	3.7	34
5-hydroxyindole	DMAP	490	3×10^7	$\sim 3 \times 10^6$	5.1	42
adrenalone	DMAP	490			~1.2	~5
HTCC	DMAP	490			2	18
p-phenylenediamine	DMAP	500	1.1×10^8	4×10^5	196	135
p-aminophenol	DMAP	490	5×10^7	1×10^7	5.3	43
7-hydroxycoumarin	DMAP	490	2.4×10^8	6×10^5	247	141
TMPD	DMAP	565	5×10^8	1×10^7	26	92
TMPD	*p*-(*N*-methylamino)phenol	565	1×10^9	1×10^7	107	120
TMPD	2,4,5-trihydroxypyrimidine	565	3×10^7		190	134
5-hydroxyindole	TMPD	565	1.1×10^8	5×10^6	15	69
5-hydroxytryptophan	TMPD	565	1.0×10^8	7×10^6	9.4	57
o-phenylenediamine	TMPD	565	2×10^9	8×10^7	22	80
o-phenylenediamine	*p*-phenylenediamine	490			8	53
p-(*N*-methylamino)-phenol	hydroquinone	430, 470	$\sim 7.5 \times 10^7$	$\sim 3 \times 10^5$	135	133
ellagic acid	hydroquinone	530	1.1×10^8	$\sim 4 \times 10^5$	600	164
quinalizarin	hydroquinone	700	2.5×10^7	3×10^6	7	50
rutin	hydroquinone	490			~10	
hydroquinone	3,4-dihydroxyphenylalanine	430			1.04	1
hydroquinone	quercetin	530	$\sim 4.5 \times 10^6$	$\sim 2 \times 10^5$	10.2	60
hydroquinone	ethyl gallate	430	3.1×10^5	2×10^4	29	77
p-(*N*-methylamino)-phenol	catechol	470	3×10^7	4.6×10^5	49	103
HTCC	catechol	430	7×10^7	3×10^5	253	142
catechol	2,5-dihydroxyphenylacetate	430	3.5×10^6	1×10^5	38	93
resorcinol	5-hydroxytryptophan	490	4×10^8	5.5×10^5	795	171
4-methoxyphenol	5-hydroxytryptophan	490	9.6×10^8	5×10^5	1920	194

One-Electron Redox Potentials

The set of redox potential differences given in Table III is used to derive the standard potentials for the one-electron oxidation of the various compounds, using the value for hydroquinone as the basic reference.[25] Table IV summarizes the results obtained in this work along with those measured by us previously.[13] Some of the earlier values have been amended and are based now on more reliable measurements and better cross-checking. The main problems were encountered with the phenylenediamines, and a few other cases, where the radicals are not sufficiently long-lived. In such cases, the electron transfer reaction leading to equilibrium is expected to be distorted by radical–radical reactions such that an erroneous K is obtained. However, examination of these cases using different (additional) reference compounds, especially those that give values of K closer to 1, allows the establishment of more reliable redox potentials.

The values summarized in Table IV were all measured at pH 13.5 and are the potentials for the ionic forms present at this pH, i.e., with most of the phenolic OH groups dissociated and the amino groups in their neutral form. Corrections for the effect of ionic strength have not been made. However, they are estimated[26] to affect the potentials by ≤20 mV depending on the charge.

The data in Table IV indicate that, while hydroquinone and catechol have similar potentials, resorcinol is much less readily oxidized, with a potential ~350 mV higher. Methylation of the O^- group also raises the potential considerably, e.g., 4-methoxyphenol has a potential 380 mV higher than that of hydroquinone. In this case the methoxyphenoxide ion at high pH has a potential close to that of hydroquinone in neutral solutions;[27] i.e., methylation of one O^- group has an effect similar in magnitude to protonation of both O^- groups in hydroquinone dianion. Phenol itself has a much higher potential, >600 mV. Introduction of OH, OCH_3, or CH_3 groups into the aromatic system renders the compound more easily oxidizable, as seen by the examples in the top part of Table IV. Acetyl or vinyl groups on the ring make oxidation more difficult, as shown by the higher potentials for dihydroxyacetophenone, adrenalone, and caffeic acid as compared with hydroquinone and catechol. All of these effects are ra-

(25) Meisel, D.; Czapski, G. *J. Phys. Chem.* **1975**, *79*, 1503.

(26) The estimates are based on the treatment given, for example, by: MacInnes, D. A. "The Principles of Electrochemistry"; Dover; New York, 1961. See also: Wardman, P.; Clarke, E. D. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1377.

(27) Ilan, Y. A.; Czapski, G.; Meisel, D. *Biochim. Biophys. Acta* **1976**, *430*, 209.

TABLE IV: One-Electron Redox Potentials[a]

compd	E, mV	reference
1,2,4-trihydroxybenzene	−110	catechol
methoxyhydroquinone	−85	catechol
ethyl gallate	−54	hydroquinone
durohydroquinone	−54	3,4-dihydroxybenzoate
2,5-dihydroxyphenylacetate (homogentisic acid)	−50	catechol
quercetin	−37	hydroquinone
pyrogallol	−9	hydroquinone
ascorbate	15	catechol
DL-β-3,4-dihydoxyphenylalanine	14	DMAP
	22	hydroquinone
3-hydroxytyramine	18	DMAP
3,4-dihydroxyphenylacetate	21	DMAP
hydroquinone	23	
2,5-dihydroxybenzoate (gentisic acid)	33	catechol
5-hydroxydopamine	42	DMAP
catechol	43	hydroquinone
DL-norepinephrine	44	DMAP
L-epicatechin	48	DMAP
DL-catechin	79	DMAP
quinalizarin	73	hydroquinone
3,4-dihydroxycinnamate	84	DMAP
2,5-dihydroxyacetophenone	118	catechol
2,3-dihydroxybenzoate	118	hydroquinone
3,4-dihdyroxybenzoate	119	hydroquinone
2,4,5-trihydroxypyrimidine	132	TMPD
p-(N-methylamino)phenol	146	catechol
	156	hydroquinone
	146	TMPD
p-(N,N-dimethylamino)phenol (DMAP)	174	hydroquinone
	174	catechol
adrenalone	~180	DMAP
6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylate (HTCC)	192	DMAP
	185	catechol
ellagic acid	187	hydroquinone
DL-5-hydroxytryptophan	208	DMAP
5-hydroxyindole	216	DMAP
	197	TMPD
p-aminophenol	217	DMAP
N,N,N′,N′-tetramethyl-p-phenylenediamine (TMPD)	266	DMAP
	265	5-hydroxytryptophan
7-hydroxycoumarin	315	DMAP
p-phenylenediamine	309	DMAP
	366	TMPD
o-phenylenediamine	346	TMPD
	360, 420	p-phenylenediamine
resorcinol	392	DMAP
	379	5-hydroxytryptophan
4-methoxyphenol	402	5-hydroxytryptophan
	~460	p-phenylenediamine
phenol	>600	resorcinol

[a] The potentials are given for reduction of the phenoxyl-type radicals, vs. NHE at room temperature (22 °C). They were all measured at pH 13.5 and calculated by using the value for hydroquinone[25] as a reference. The experimental error limits are usually ±10 mV.

tionalized on the basis of the electron-donating or -withdrawing properties of the substituents as may be expressed by Hammett's substituent constants. Hammond et al.[28] have previously correlated the antioxidant activity of a series of phenols with the Hammett σ values.

Anilines are more difficult to oxidize than phenoxide ions. In going from hydroquinone to p-aminophenol to p-phenylenediamine, the potential increases from 23 to 217 to ~340 mV. Dimethylation of the amino group lowers the potential by nearly 50 mV; compare, e.g., TMPD with p-phenylenediamine and DMAP with p-aminophenol. Monomethylation may be expected to have an intermediate effect, but the results for p-(N-methylamino)phenol show a value which is lower than those of either p-aminophenol or DMAP. The reason for this apparent discrepancy is unclear.

TABLE V: One-Electron Redox Potentials in Alkaline and Neutral Solutions

compd	E, V pH 13.5	E, V pH 7[a]
ascorbate	0.015	0.30
hydroquinone	0.023[b]	0.459[b]
catechol	0.043	0.53
resorcinol	0.385	0.81
HTCC	0.192	0.48
p-methoxyphenol	0.40	0.60
phenol	>0.60	>0.80
p-aminophenol	0.22	0.41
p-phenylenediamine	0.34	0.73
TMPD	0.27	0.27

[a] Calculaed from the experimental values at pH 13.5 by using the equation given in ref 13, Table IV, and ref 27. The pK_a values of the compounds were taken from: Kortum, G.; Vogel, W.; Andrussow, K. "Dissociation Constants of Organic Acids in Aqueous Solution"; Butterworths, London, 1961. Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths, London, 1965. For HTCC pK_a = 11.92 was determined by: Steenken, S., unpublished result. The pK_a values of the radicals were taken from ref 15 and from: Steenken, S.; O'Neill, P. *J. Phys. Chem.* **1977**, *81*, 505. Laroff, G. P.; Fessenden, R. W.; Schuler, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 9062. [b] From ref 27.

Several biologically important catechols and catecholamines were examined, and their potentials are found to be very similar to that of catechol itself, except for adrenalone, which is deactivated by the carbonyl group. 5-Hydroxyindole and 5-hydroxytryptophan have very similar redox potentials, and these are close to the value of p-aminophenol, as expected from the similarity in their basic structures. Since serotonin has a similar structure, it is expected to have a redox potential of ~200 mV at high pH.

Quercetin, because of its 3′- and 4′-OH groups, resembles catechol. The 3-OH group on the other ring is conjugated with the catechol portion and thus lowers the potentials by ~80 mV as compared with catechol itself, while the 5- and 7-OH groups probably do not take part in the oxidation process. Quinalizarin has both a catechol and a hydroquinone ring, but they are both deactivated by the central carbonyl groups which raise the potential to 73 mV.

Isobarbituric acid exhibits a redox potential ~240 mV higher than that of 1,2,4-trihydroxybenzene. Since the three OH groups in both compounds have the same configuration, the difference in potential can be assigned to the electron-withdrawing effect of the two nitrogens in the ring of the isobarbiturate.

HTCC is a water-soluble analogue of vitamin E. The potential of 190 mV measured for the former should be a good measure for the latter as well. This value is much higher than that (15 mV) measured for ascorbate, and a similar situation exists at pH 7 as well (see below). This difference is in line with the recent finding[29] that vitamin E radicals are repaired by vitamin C, and also explains the

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synergistic effect of ascorbate on the antioxidation activity of α-tocopherol.[30]

The redox potentials reported in Table IV were measured at high pH. Direct measurement in neutral or acid solutions is made impossible by the very low rates of electron transfer reactions involving the undissociated phenols.[13] Nevertheless, the values measured in the present work can be used to calculate the potentials in neutral and acid solutions if the pK_a values of the compound and its radical are known. Such calculations for ascorbic acid and the three dihydroxybenzenes have been reported earlier.[13] Table V summarizes the redox potentials at pH 7 and 13.5 for several compounds for which the pK_a values are known. In the case of TMPD, where both the compound and its radical do not undergo any acid-base equilibria between pH 7 and 13.5 and where the redox reaction studied does not involve any proton transfer, the potential is the same at both pH values. With all of the other compounds in Table V, the potential changes to an extent which depends on the pK_a values, and as a result the relative oxidizabilities of the compounds change. For instance, at pH 13.5 ascorbate, hydroquinone, and catechol are much more easily oxidized than TMPD, whereas at pH 7 TMPD is the most powerful reductant in this group.

In conclusion, rapid one-electron transfer processes between various phenoxyl radicals and phenoxide ions, and the corresponding amino derivatives, have been observed by kinetic spectrophotometry. Analysis of the rates and equilibria led to the determination of one-electron oxidation potentials for the various compounds studied. Some of these compounds are of importance as antioxidants or as components of biological systems, possibly involved in electron transfer reactions. The knowledge of their redox potentials may help to achieve a better understanding of their function and may be useful in predicting redox potentials for similar compounds which are not easily accessible.

(30) Reference 3, p 207.

Investigation of the Hydrolysis of Aqueous Solutions of Aluminum Chloride. 2. Nature and Structure by Small-Angle X-ray Scattering

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The process of hydrolysis-precipitation of aluminum from aqueous aluminum chloride solution at 25 °C and for a concentration of 10^{-1} M has been studied by using solutions with a neutralization ratio $r = (NaOH)/(Al_T)$ equal to 2 and 2.5, by small-angle X-ray scattering using a synchrotron source. In the former case, the aluminum ion is embodied principally in a polymer with the formula $Al_{13}O_4(OH)_{28}^{3+}$ with an experimental radius of gyration of 9.8 Å, which corresponds to an ionic radius of 12.6 Å. In the second case, the aluminum is embodied partly in the species described above and partly in a colloidal species of chemical composition similar to that of the trihydroxide. The particle morphology of the colloidal species changes as a function of time. After aging for 1.5 h, the particles are cylindrical with a radius of about 15 Å and a length of 310 Å. After 24-h aging, the cylinders have agglomerated into more homogeneous platelets of diameter 500 Å and thickness 60 Å.

Introduction

Aluminum chemistry is of considerable interest in geoscience and water treatment. Many authors have interpreted their results in terms of Al^{3+} ion hydrolysis in acidic medium with the "core + links" theory.[1,2] This theory leads one to conceive, according to the neutralization ratio $r = (NaOH)/(Al_T)$, where the parentheses indicate the total sodium hydroxide and aluminum concentrations, a series of polymers the growth of which is bidimensional[3-9] and whose basic structure is a six-aluminum ring whose formula is $Al_6(OH)_{12}^{6+}$.

Some authors[1,3] suggest the existence of large, two-dimensional polymers able to contain more than 1000 atoms of aluminum. It appears that this growth model is not accepted by some authors[10] for systems such as chromia gels. According to these authors, growth along the C axis takes place immediately as a certain molecular weight is exceeded.

In an earlier publication,[11] we reported finding by ^{27}Al NMR and potentiometric titration five species in dilute solutions ($(Al_T) = 10^{-1}$ M) according to the neutralization ratio $r = (NaOH)/(Al_T)$: the monomers $Al(H_2O)_6^{3+}$, $Al(H_2O)_5(OH)^{2+}$, $Al(H_2O)_4(OH)_2^{+}$; a dimer $Al_2(OH)_2^{4+}$; a

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