substituents in the gas phase are reduced by factors of 2–4 in Me_2SO by larger effective dielectric constants. The 11 kcal decrease in solution acidity caused by introducing a t-Bu group into $CH_2(CO_2Et)_2$ is revealed by the $\delta_s\Delta G°$ value to be caused by steric inhibition of solvation of the carbanions. π delocalization of the anionic charge by the presence of a Ph substituent at the acidic site causes large increases in acidity, but the effects of successive Ph substitutions are decreased appreciably by leveling (saturation) effects and by steric inhibition of resonance in both media. The surprisingly small acidity increase in solution acidity for Ph_3CH vs Ph_2CH_2 (2.5 vs 5.4 kcal in the gas phase) is the result of a 3 kcal greater solvation energy for the Ph_2CH^- than the Ph_3C^- carbanion.

The solution order of acidities, cyclopentadiene > indene > fluorene, first reported over 50 years ago[15] is shown to be caused by striking differences in the anion solvation energies (11.7, 5.8, and 1.8 kcal, relative to 9-phenylfluorenide ion) that cause a reversal from the intrinsic acidity order. Solvation of substituent sites to which a significant fraction of anionic charge has been relayed by resonance (SSAR effects) is shown to be responsible for the dramatic near equalization of the solution acidities of p-nitrotoluene and p-nitroaniline. The SSAR effects are general and play important roles, not only in determining solution equilibrium positions but also in controlling reaction rates and physical properties.

Hydroxide Ion: An Effective One-Electron Reducing Agent?

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The reaction chemistry for hydroxide ion ($^-$OH) includes Brønsted proton transfer, nucleophilic displacement (or addition), and electron transfer whereby $^-$OH acts as a one-electron reducing agent.[1] In this Account, via examples from our own work and that of others, the reactivity of hydroxide ion (and by implication that of other anions) is interpreted in terms of two unifying principles: (a) the redox potential of the $^-$OH/$^•$OH couple (in a specific reaction) is controlled by the solvation energy of the $^-$OH anion and the bond energy of the R–OH product (RX + $^-$OH → R–OH + X$^-$), and (b) the nucleophilic displacement and addition reactions of $^-$OH occur via an inner-sphere *single-electron* shift.[2]

The electron is the ultimate base and one-electron reductant, which, upon introduction into a solvent, is transiently solvated before it is "leveled" (reacts) to give the conjugate base (anion reductant) of the solvent. Thus, in water the hydrated electron $(e^-)_{H_2O}$ yields $^-$OH via addition to the H–OH bond of water.[3]

$$(e^-)_{H_2O} + H–OH \rightarrow H^• + (^-OH)_{H_2O}$$
$$E° = -2.93 \text{ V vs NHE} \quad (1)$$
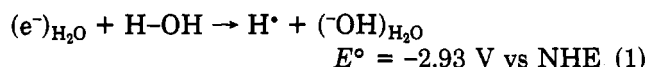
The product combination ($H^•$ + $^-$OH) represents the ultimate thermodynamic reductant for aqueous systems. In the absence of an $H^•$ atom (and the stabilization afforded to $^•$OH by formation of the 119-kcal H–OH bond),[4] the hydroxide ion becomes a much less effective reductant.[3]

$$(e^-)_{H_2O} + {}^•OH \rightarrow (^-OH)_{H_2O}$$
$$E° = +1.89 \text{ V vs NHE} \quad (2)$$
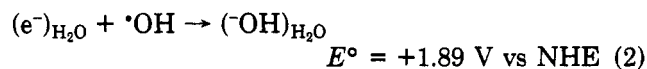
Solvent Effects on the Redox Chemistry of $^-$OH

Table I summarizes the redox potentials in water and acetonitrile for the single-electron oxidation of $^-$OH and other bases.[3,5] In MeCN the $HO^•/HO^-$ redox potential is more negative by about 1.0 V and the $O_2/O_2^{•-}$ redox potential by about 0.5 V relative to their values in H_2O. Most of this is due to the decrease in the energy of solvation for HO^- and $O_2^{•-}$ in MeCN (compared to water, where each has an estimated free energy of hydration of about -100 kcal/mol).[6] The increase in the ionization energy for $^-$OH from 1.8 eV in the gas phase to 6.2 eV in water[6] attests to its large solvation energy and to its dramatic deactivation as a base and nucleophile in water.[7,8]

(1) Fomin, G. V.; Blyumenfel'd, L. A.; Sukhorukov, V. I. *Dokl. Akad Nauk SSSR* **1964**, *157*, 819.
(2) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.
(3) (a) Parsons, R. *Handbook of Electrochemical Constants*; Butterworths: London, 1959; pp 69–73. (b) Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.
(4) *CRC Handbook of Chemistry and Physics*, 68th ed.; CRC: Boca Raton, FL, 1987; pp F-168–181.
(5) Tsang, P. K. S.; Cofré, P.; Sawyer, D. T. *Inorg. Chem.* **1987**, *26*, 3604.
(6) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.
(7) (a) Bohme, D. K.; Mackay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 978. (b) Tanner, S. D.; Mackay, G. I.; Bohme, D. K. *Can. J. Chem.* **1981**, *59*, 1615. (c) Evanseck, J. D.; Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1987**, *109*, 2349.

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Table I
Redox Potentials for the Single-Electron Oxidation of ⁻OH and Other Bases and the Single-Electron Reduction of Electrophilic Substrates

A. Oxidation of Bases

base (:B⁻)	$(pK_{HB})_{H_2O}{}^a$	$E^{o'}{}_B$, V vs NHE $(:B^- \to B^\cdot + e^-)$ H₂O calcd[b]	measd[c]	MeCN[d]
⁻OH → ·OH + e⁻	15.7	+1.72	+1.89	+0.92 (+0.96)[b]
2⁻OH → O·⁻ + H₂O + e⁻	15.7		+1.77	+0.59
MeO⁻ → MeO· + e⁻	18.0	+1.10		
PhO⁻ → PhO· + e⁻	9.9	+0.92		+0.30
O₂·⁻ → ·O₂· + e⁻	4.9	−0.19	−0.16[e]	−0.66 (−0.66)[b,e]
HO₂⁻ → HOO· + e⁻	11.7	+0.83		+0.64
Cl⁻ → Cl· + e⁻	−8	+2.31	+2.41	+2.24
CN⁻ → ·CN + e⁻	9.3	+2.52		
PhNH₂ → PhNH₂·⁺ + e⁻	4.6	+0.03		
Me₃N → Me₃N·⁺ + e⁻	9.9	+0.71		

B. Reduction of Electrophiles

electrophile (XY)	X–OH bond energy,[f] kcal	$E^{o'}{}_E$, V vs NHE $[XY + e^- \to XY^{\cdot-}$ (or $X^\cdot + Y^-)]$ H₂O[c]	MeCN
H₃O⁺ + e⁻ → H· + H₂O	119	−2.10	−1.58
BuCl + e⁻ → Bu· + Cl⁻	91		−2.5
CCl₄ + e⁻ → ·CCl₃ + Cl⁻	80		−0.91
AQ + e⁻ → AQ·⁻	80		−0.58
2-Et-AQ + e⁻ → 2-Et-AQ·⁻	80		−0.7
MV²⁺ + e⁻ → MV·⁺	80	−0.45	−0.18
BV²⁺ + e⁻ → BV·⁺	80	−0.36	−0.08
Au⁺ + e⁻ → Au·	37	+1.7	+1.58
(TPP)Fe^III(py)₂⁺ + e⁻ → (TPP)Fe^II(py) + py			+0.38
(TPP)Mn^III(ClO₄) + e⁻ → (TPP)Mn^II + ClO₄⁻			+0.1

^{a} pK_a of the conjugate acid.[6] ^{b} Calculated from the relation $[E^{o'} = I − 4.50]$, where I is the ionization potential.[6] ^{c} Reference 3. ^{d} Reference 5. ^{e} Standard state for O₂ is 1 M. ^{f} Reference 4.

Hydroxide ion is a stronger base and a better one-electron donor in MeCN and Me₂SO than in water, because these organic solvents have solvation energies for ⁻OH that are 20–25 kcal mol⁻¹ (~1 eV) less than that in water.[9] Thus, reduced solvation of ⁻OH decreases its ionization energy and causes it to have a more negative redox potential and to be a stronger electron donor. (The solvation energies of the HO· radical and neutral molecules are small,[6] so that the large changes in redox potential are due primarily to the solvation of anions.) This dramatically enhances the reactivity of HO⁻ toward the electrophiles shown in Table IB and reveals a facet of ⁻OH chemistry that is effectively quenched by water, namely its ability to function as a one-electron reducing agent.

The redox potentials for the electron acceptors that react with HO⁻ (Table IB) are such that a pure outer-sphere SET step would be endergonic (the HO·/HO⁻ redox potential is more positive than the redox potential of the electron acceptor). Hence, the observed net reactions must be driven by coupled chemical reactions, particularly bond formation by the HO· to the electrophilic atom of the acceptor molecule, that accompany a single-electron shift. (The formation of the bond provides a driving force sufficient to make the overall

(8) Landini, D.; Maia, A. *J. Chem. Soc., Chem. Commun.* 1984, 1041.
(9) Popovych, O.; Tomkins, R. P. T. *Nonaqueous Solution Chemistry*; Wiley: New York, 1981; Chapter 10.

Table II
Oxidation Potentials for ⁻OH in H₂O and MeCN and in the Presence of Metal Complexes

	$E^{o'}$, V vs NHE	
	H₂O	MeCN
A. Free Base		
⁻OH → ·OH + e⁻	+1.89	+0.92
2⁻OH → O·⁻ + H₂O + e⁻	+1.77	+0.59
2⁻OH → O(g) + H₂O + 2e⁻	+1.60	+0.63
3⁻OH → HO₂⁻ + H₂O + 2e⁻	+0.87	−0.11
B. Metal–Porphyrin Complexes		
(TPP)Zn^II(⁻OH)⁻ + ⁻OH → (TPP)Zn^II(O·⁻)⁻ + H₂O + e⁻		+0.73
(TPP)Co^II(⁻OH)⁻ + ⁻OH → (TPP)Co^II(·O⁻) + H₂O + e⁻		+0.02
(TPP)Fe^III(⁻OH) → (TPP)Fe^III(·OH)⁺ + e⁻		+1.19
(TPP)Fe^III(⁻OH)₂⁻ + ⁻OH → (TPP)Fe^III(·O⁻)(⁻OH)⁻ + H₂O + e⁻		+0.03
(TPP)Mn^III(⁻OH)₂²⁻ + ⁻OH → (TPP)Mn^III(·O⁻)(⁻OH)⁻ + H₂O + e⁻		−0.35
C. Metal–(Ph₃PO) Complexes		
(Ph₃PO)₄Zn^II(⁻OH)₂ + ⁻OH → (Ph₃PO)₄Zn^II(⁻OH)(O·⁻) + H₂O + e⁻		+0.67
(Ph₃PO)₄Ni^II(⁻OH)₂ + ⁻OH → (Ph₃PO)₄Ni^II(·O⁻)(⁻OH) + H₂O + e⁻		−0.01
(Ph₃PO)₄Co^II(⁻OH)₂ + ⁻OH → (Ph₃PO)₄Co^II(·O⁻)(⁻OH) + H₂O + e⁻		−0.05
(Ph₃PO)₄Fe^II(⁻OH)₂ + ⁻OH → (Ph₃PO)Fe^II(·O⁻)(⁻OH) + H₂O + e⁻		+0.12
(Ph₃PO)₄Mn^II(⁻OH)₂ + ⁻OH → (Ph₃PO)₄Mn^II(·O⁻)(⁻OH) + H₂O + e⁻		+0.31

Scheme I
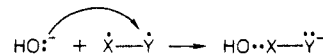**Single-Electron Shift (Equivalent to the Transfer of an Electron from O to Y)**

O ⟶ Y

single-electron shift

1. Polar–group transfer (e.g., a Brønsted proton–transfer reaction or a nucleophilic–displacement reaction)

HO:⁻ + X··Y ⟶ HO··X + :Y⁻
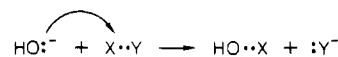
2. Polar–group coupling (e.g., a nucleophilic–addition reaction to a double bond; X = C, Y = O)

HO:⁻ + X̲—Y̲ ⟶ HO··X—Ÿ⁻

3. Single-electron transfer (SET)

HO:⁻ + X—Y ⟶ HO· + (X—Y)·⁻

reaction thermoneutral or exergonic; 1.0 V per 23.1 kcal of bond energy.) A recent study of the effect of various transition-metal complexes on the oxidation potential for ⁻OH in MeCN illustrates some of these effects; the results are summarized in Table II.[5]

In organic solvents the HO· radical that is produced by an SET step also may be captured by the solvent or dimerize to form hydrogen peroxide, HOOH. Bona fide examples of the latter reaction are rare because the competing reaction with solvent is faster, except perhaps in MeCN.[10] Second, hydrogen peroxide is highly reactive in basic solutions of dipolar aprotic solvents, including MeCN.[11] Thus, hydrogen peroxide may not be found, even if it is produced at some stage of the

(10) (a) Ross, F.; Ross, A. B., Eds. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand (U.S.)* 1977, 59. (b) Walling, C. *Acc. Chem. Res.* 1975, 8, 125. (c) Kunai, A.; Hata, S.; Ito, S.; Sasaki, K. *j. Am. Chem. Soc.* 1986, 108, 6012.
(11) (a) Roberts, J. L., Jr.; Morrison, M. M.; Sawyer, D. T. *J. Am. Chem. Soc.* 1978, 100, 329. (b) Sawaki, Y.; Ogata, *Bull. Chem. Soc. Jpn.* 1981, 54, 793. (c) Payne, G. B.; Deming, P. H.; Williams, P. H. *J. Org. Chem.* 1961, 26, 659.

Scheme II
Redox Energetics for Single-Electron-Shift Reactions

	energy change, J
electron donor: $HO:^- \rightarrow HO^\bullet + e^-$	$-(E^{\circ\prime}_{HO^\bullet/HO^-})nF$
electron acceptor: $X-Y + e^- \rightarrow$ $X-Y^{\bullet-} \rightarrow X^\bullet + Y:^-$	$(E^{\circ\prime}_{XY/XY^{\bullet-}})nF$
bond formation: $HO^\bullet + X^\bullet \rightarrow HO-X$	$(BE_{HO-X})nF/23.1$

polar-group transfer
$HO:^- + X-Y \rightarrow HO-X + Y:^-$
$\quad -\Delta G_{reac} = nF[(E^{\circ\prime}_{XY/XY^{\bullet-}} - E^{\circ\prime}_{HO^\bullet/HO^-}) + (BE_{HO-X}/23.1)] = nF[\Delta E^{\circ\prime}_{reac} + (BE_{HO-X}/23.1)]$

polar-group coupling
$HO:^- + X-Y \rightarrow HO:X:Y^-$
$\quad -\Delta G_{reac} = nF[\Delta E^{\circ\prime}_{reac} + (BE_{HO-XY}/23.1)]$

single-electron transfer (SET)
$HO:^- + X-Y \rightarrow HO^\bullet + X-Y^{\bullet-}$
$\quad -\Delta G_{reac} = nF\Delta E^{\circ\prime}_{reac}$

reaction. For systems in which hydrogen peroxide is suspected, the formation of dioxygen or oxygenated products may be used as indirect evidence of its intermediacy.

Reaction Classifications (Single-Electron-Shift Mechanism)

The reaction continuum for ^-OH can be subdivided into three discrete categories that are outlined in Scheme I: (1) displacement reactions in which the leaving group departs with an electron supplied by ^-OH (polar-group transfer), (2) addition reactions in which a covalent bond is formed (polar-group addition), and (3) simple electron-transfer reactions in which ^-OH acts as an electron donor (single-electron transfer). This view of the chemistry of ^-OH also applies to the reactions of superoxide ion ($O_2^{\bullet-}$) and other nucleophilic anions (Table IA).

The polar pathways are formally equivalent to a discrete electron-transfer step, i.e., a pure SET step that is followed by a chemical step. If a hypothetical SET step is followed by coupling of a free-radical pair that is produced in the SET step, the overall reaction is the equivalent of a polar-group-coupling reaction (reaction 2 of Scheme I). If the coupling is accompanied by the elimination of a leaving group, a polar-group-transfer reaction results (reaction 1 of Scheme I).

The "single-electron-shift" mechanism appears to be general and applicable for electron-, proton-, atom-, and group-transfer reactions. The assumptions for this proposition include the following: (a) Polar and SET pathways share a common feature, a single-electron shift from an electron donor to an electron acceptor. (b) The barrier heights for the exchange of an electron, proton, atom, or group of atoms can be described by the same general equation.[12] (c) For an unsymmetrical polar-group-transfer reaction the net energy change, ΔG (the thermodynamic component of the energy barrier), is proportional to the sum of (i) the difference of the redox potentials for the electron acceptor (X–Y) and the electron donor (HO:$^-$) and (ii) the bond energy (BE) for the group-transfer product (HO–X; see Scheme II).

Table III lists a number of reactions of hydroxide ion and, for comparison, superoxide ion with electron donors. These reactions are classified conventionally and according to the categories shown in Scheme I. When water is replaced by a dipolar aprotic solvent [e.g., acetonitrile (MeCN) or dimethyl sulfoxide (Me$_2$SO)], many of these electron donor–electron acceptor reac-

Table III
Reactions of Hydroxide Ion and Superoxide Ion with Electrophiles

1. Polar-Group-Transfer Reactions
   a. Deprotonation by Hydroxide ion
      $HO^- + H_3O^+ \rightarrow 2H_2O$
      $HO^- + CH_3OH \rightarrow H_2O + CH_3O^-$
      $HO^- + HOC(O)R \rightarrow H_2O + {}^-OC(O)R$
      $O_2^{\bullet-} + NH_4^+ \rightarrow HOO^\bullet + NH_3$
      $O_2^{\bullet-} + HOCH_3 \rightarrow HOO^\bullet + CH_3O^-$
   b. Nucleophilic Substitution Reactions
      $HO^- + RCl \rightarrow ROH + Cl^-$
      $O_2^{\bullet-} + RCl \rightarrow ROO^\bullet + Cl^-$
      $HO^- + RC(O)OR' \rightarrow RC(O)O^- + ROH$
      $O_2^{\bullet-} + RC(O)OR' \rightarrow RC(O)OO^\bullet + RO^-$
      $4HO^- + CCl_4 \rightarrow 3Cl^- + ClC(O)O^- + 2H_2O$
      $5O_2^{\bullet-} + CCl_4 + H_2O \rightarrow 4Cl^- + HOC(O)O^- + {}^7/_2O_2 + {}^1/_2HOOH$
2. Polar-Group-Coupling Reactions
   a. Nucleophilic Addition Reactions
      $HO^- + CO_2 \rightarrow HOC(O)O^-$
      $O_2^{\bullet-} + CO_2 \rightarrow {}^\bullet OOC(O)O^-$
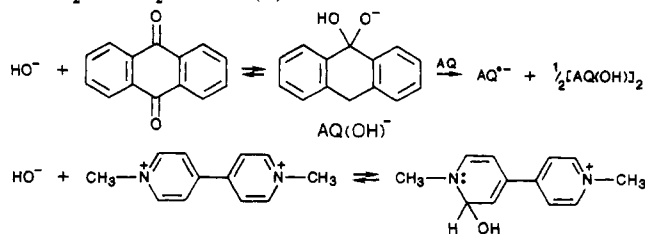
   b. Reductive Addition Reactions
      $HO^- + Au^+ \rightarrow Au-OH$
      $HO^- + Fe^{III}(TPP)^+ \rightarrow (TPP)Fe-OH$
      $HO^- + Fe^{III}(TPP)(py)_2^+ \rightarrow Fe^{II}(TPP) + {}^1/_n[py(^\bullet OH)]_n$
      other $M^{III}/^-OH$ reactions
3. Single-Electron-Transfer Reactions

$HO^- + O_2 \xrightarrow{py} O_2^{\bullet-} + {}^1/_n[py(^\bullet OH)]_n$
$HO^- + (CN)_2C=C(CN)_2 \rightarrow [(CN)_2C=C(CN)_2]^{\bullet-} + {}^1/_2HOOH$
$HO^- + S_8 \rightarrow HOS_8^\bullet + S_3^{\bullet-}$
$\quad \xrightarrow{^-OH} HOSSOH + S_3^{\bullet-}$
$\quad \rightarrow HOOH + {}^1/_4S_8$
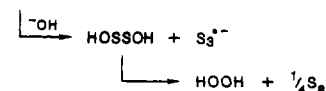
tions proceed at dramatically faster rates and produce much larger yields of free-radical products. [Dimethylformamide (DMF) is generally avoided because of the possible hydrolysis of the amide bond by hydroxide ion.[13]]

As the prototype reactions in Scheme I imply, a reaction that involves a single-electron shift may not produce observable free-radical products. Conversely, the failure to find free-radical products does not prove the absence of a single-electron-shift mechanism. Other arguments are necessary to establish the nature of polar-group-transfer and polar-coupling reactions.

Polar-Group-Transfer Reactions

Deprotonation by Hydroxide Ion. Although Brønsted proton-transfer reactions appear to belong to a unique category not described by Scheme I, we believe that they are examples of polar-group-transfer reactions and are not different in principle from nucleophilic

(12) Murdoch, J. R. *J. Am. Chem. Soc.* 1983, *105*, 2159.

(13) Buncel, E.; Kesmarky, S.; Symons, E. A. *J. Chem. Soc., Chem. Commun.* 1971, 120.
(14) (a) Mullay, J. *J. Am. Chem. Soc.* 1986, *108*, 1770. (b) Jug, K.; Epiotis, N. D.; Buss, S. *J. Am. Chem. Soc.* 1986, *108*, 3640. (c) Sanderson, R. T. *Polar Covalence*; Academic: New York, 1983; pp 181, 194.

displacement reactions. Deprotonation by hydroxide ion can be regarded as the shift of an electron from HO^- to the Brønsted acid synchronously with the transfer of a hydrogen atom from the Brønsted acid to the incipient $HO^•$ radical, with the reaction driven by covalent bond formation between the $HO^•$ radical and the $H^•$ atom to form water.

$$HO{:}^- + H^{••}B \rightleftharpoons [HO{\cdots}H{:}B^-] \rightleftharpoons$$
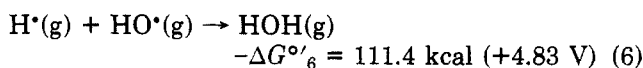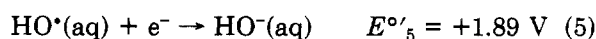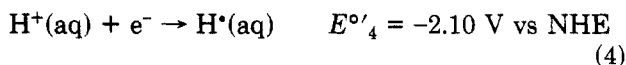$$HO{:}H + B{:}^- \qquad BE_{HO-H}=119 \text{ kcal} \quad (3)$$
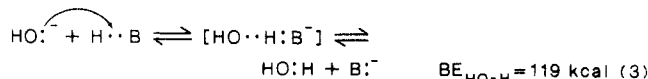
Consistent with the idea that the single-electron shift is a fundamental process is the notion that the electron distribution (or partial charge) on atoms near the reaction site changes during the course of the reaction. This is so obvious as to seem trivial, but bears repeating because our thinking often is misdirected by the assignment of oxidation numbers (or oxidation states) to atoms via arbitrary rules. For example, by convention the oxidation state $+1$ is assigned to the hydrogen and -2 is assigned to the oxygen in hydronium ion, water, and hydroxide ion. However, the partial charges on the hydrogen and oxygen atoms change substantially in this series: H_3O^+ ($+0.35$, -0.05); H_2O ($+0.12$, -0.25); and HO^- (-0.35, -0.65).[17]
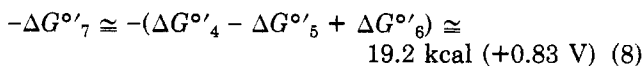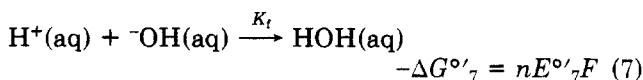
In the present discussion we use the term "charge number" to represent more accurately the partial charge on an atom and define the charge number as the nearest integer value of the partial charge on an atom. Thus, in ^-OH the hydrogen is "zero-charge" and the oxygen "-1 charge", and in water both hydrogen and oxygen are zero charge. For H_3O^+ the partial charge distributed over the three equivalent hydrogen atoms is assigned to a single hydrogen atom ($+1$-charge hydrogen) and the oxygen atom is zero charge.

From Scheme I and the notion of the charge number (or partial charge on an atom), the reaction of hydroxide ion (-1-charge oxygen) with a proton ($+1$ charge) to form H_2O (zero-charge H and O) involves a single-electron-shift from HO^- to $H^+(H_2O)$ to form $HO^•$ and $^•H(H_2O)$ that form a covalent bond ($HO-H$) with a bond energy of 119 kcal/mol.[4] This reaction does not result in the formation of detectable free radical, but is an example of a polar-group-transfer reaction (reaction 2 of Scheme I) in which an atom transfer occurs synchronously with the electron shift.

Thus, the reaction of H^+ with ^-OH is a prototype example of a charge-transfer or redox reaction that is also a polar-group-transfer reaction. It can be resolved into three component reactions (see Scheme II):
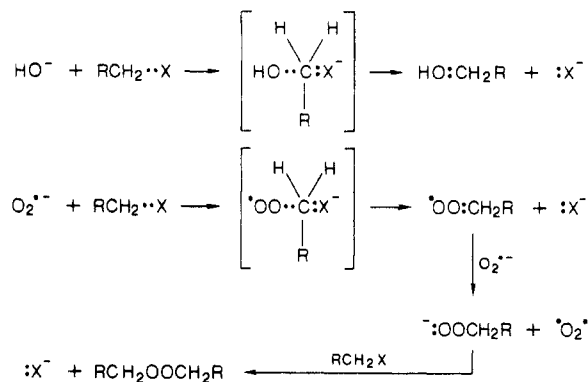
$$H^+(aq) + e^- \rightarrow H^•(aq) \qquad E°'_4 = -2.10 \text{ V vs NHE} \tag{4}$$

$$HO^•(aq) + e^- \rightarrow HO^-(aq) \qquad E°'_5 = +1.89 \text{ V} \tag{5}$$

$$H^•(g) + HO^•(g) \rightarrow HOH(g)$$
$$-\Delta G°'_6 = 111.4 \text{ kcal } (+4.83 \text{ V}) \tag{6}$$

These can be combined (eq 4 – eq 5 + eq 6) to give

$$H^+(aq) + {}^-OH(aq) \xrightarrow{K_t} HOH(aq)$$
$$-\Delta G°'_7 = nE°'_7F \tag{7}$$

$$-\Delta G°'_7 \cong -(\Delta G°'_4 - \Delta G°'_5 + \Delta G°'_6) \cong$$
$$19.2 \text{ kcal } (+0.83 \text{ V}) \tag{8}$$

The latter neglects the small differences in the hydra-

Scheme III
Nucleophilic Substitution

tion energies of $H^•$, $HO^•$, and H_2O, but provides a reasonable measure of the formation constant (K_f):

$$\log K_f \cong +0.83/0.059 \cong 14 \tag{9}$$

In the net reaction (eq 7) the energy from bond formation (eq 6) provides a driving force of nearly 5 V, which is more than sufficient to overcome the unfavorable electron-transfer energy.

The reaction of superoxide ion ($O_2^{•-}$), a radical anion, with water also can be viewed as a polar-group-transfer reaction:

$$^•OO{:}^- + H{:}OH \rightleftharpoons [^•OO{:}H{:}^-OH] \rightleftharpoons {}^•OO{:}H + {}^-OH \tag{10}$$
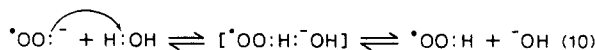
Here the product $HO_2^•$ is a free radical that reacts bimolecularly to form hydrogen peroxide and dioxygen.

$$2HO_2^• \rightarrow HOOH + O_2 \tag{11}$$
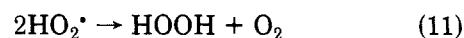
The formation of the stable covalent bonds in the product molecules provides the driving force that allows superoxide to deprotonate Brønsted acids that are much weaker acids than $HO_2^•$.

Because every chemical reaction involves charge transfer (or at least partial electron shifts), the distinction between an acid–base reaction and an oxidation–reduction reaction becomes meaningless unless defined in terms of changes in conventionally assigned oxidation number.[15] This point of view also has been expressed before, but still is not discussed in contemporary textbooks of general, organic, and inorganic chemistry.

Nucleophilic Substitution Reactions. The view that substitution or displacement reactions that involve hydroxide ion are examples of polar-group-transfer reactions (with a single-electron shift) is probably the least iconoclastic proposal. Most accept the view that many nucleophilic displacement reactions occur by a SET mechanism.[16] In a number of cases free-radical intermediates have been identified, which is consistent with a discrete SET step. Only a slight extension of this concept is required to encompass all nucleophilic reactions within the categories described in Scheme I.

The reactions of HO^- and $O_2^{•-}$ with alkyl halides exhibit the same general pattern (Scheme III), with second-order kinetics and inversion of configuration.[17]
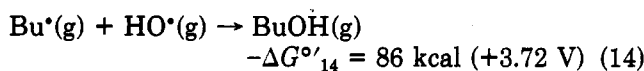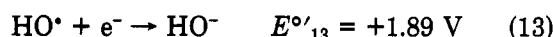
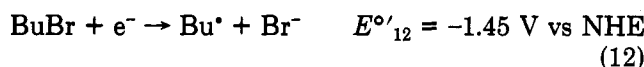(15) Sisler, H. H.; Vanderwerf, C. A. *J. Chem. Educ.* **1980**, *57*, 42.

(16) (a) Blyumenfel'd, L. A.; Bryukhovetskaya, L. V.; Fomin, G. V.; Shein, S. M. *Russ. J. Phys. Chem. (Engl. Transl.)* **1970**, *44*, 518. (b) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1. (c) Chanon, M. *Bull. Chim. Soc. Fr.* **1982**, II-197. (d) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

Free radicals are not detected in the reactions with hydroxide, which indicates that there probably is not a discrete SET step, but rather that the transfer of the entering and leaving groups is synchronous with a single-electron shift.

The reaction of superoxide ion with alkyl halides produces a free radical in the primary step, because the spin angular momentum of the unpaired electron of the superoxide anion radical is conserved. Again, the transfer of the entering and leaving group is presumed to be synchronous with the single-electron shift. The alternative mechanism, a discrete SET step followed by expulsion of the leaving group and coupling of the radical with dioxygen, is implausible because the reduction potentials of most alkyl halides are at least 0.8 V more negative than the $O_2/O_2^{\cdot-}$ redox potential and the formation of alkyl radicals has not been observed.

Thus, the reaction of ^-OH with BuBr is another example of a redox reaction that involves a polar-group transfer. This can be resolved into three component reactions (in MeCN):

$$BuBr + e^- \rightarrow Bu^\cdot + Br^- \qquad E^{\circ\prime}_{12} = -1.45 \text{ V vs NHE} \tag{12}$$

$$HO^\cdot + e^- \rightarrow HO^- \qquad E^{\circ\prime}_{13} = +1.89 \text{ V} \tag{13}$$

$$Bu^\cdot(g) + HO^\cdot(g) \rightarrow BuOH(g)$$
$$-\Delta G^{\circ\prime}_{14} = 86 \text{ kcal } (+3.72 \text{ V}) \tag{14}$$

These can be combined (eq 12 − eq 13 + eq 14) to give

$$BuBr + {}^-OH \rightarrow BuOH + Br^- \qquad -\Delta G^{\circ\prime}_{15} = nE^{\circ\prime}_{15}F \tag{15}$$
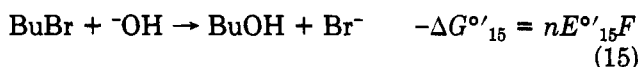
$$-\Delta G^{\circ\prime}_{15} = -(\Delta G^{\circ\prime}_{12} - \Delta G^{\circ\prime}_{13} + \Delta G^{\circ\prime}_{14}) \approx 8.8 \text{ kcal } (+0.38 \text{ V}) \tag{16}$$

Similar analyses are possible for the initial polar-group-transfer step for CCl_4 ($E^{\circ\prime}_{red} = -0.90$ V vs NHE), C_6Cl_6 ($E^{\circ\prime}_{red} = -1.26$ V), and $C_{12}Cl_{10}$ (PCB; $E^{\circ\prime}_{red} = -1.30$ V). Each of these substrates undergoes a net exergonic redox reaction with ^-OH with an initial step analogous to that of eq 15.

The reactions of CCl_4 with HO^- and $O_2^{\cdot-}$ are complex multistep reactions, and the nature of the primary step is not well understood. The primary reaction step is followed by even faster secondary reactions that ultimately result in the almost complete oxygenation of the carbon and the release of the chlorine as chloride ion. The overall reaction for superoxide ion with CCl_4 (followed by dilution with water)

$$5O_2^{\cdot-} + CCl_4 + H_2O \rightarrow$$
$$HOC(O)O^- + 4Cl^- + \tfrac{7}{2}O_2 + \tfrac{1}{2}H_2O_2 \tag{17}$$
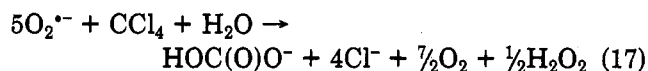
results in the stoichiometric formation of bicarbonate ion.[18] The reaction of hydroxide ion with CCl_4 in dimethyl sulfoxide (followed by dilution with water) has a net stoichiometry that is consistent with the reaction

$$4HO^- + CCl_4 \rightarrow ClC(O)O^- + 3Cl^- + 2H_2O \tag{18}$$
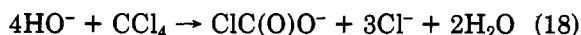
(without positive identification of chloroformate ion).[19]

(17) (a) San Filipo, J., Jr.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* 1975, 40, 1678. (b) Johnson, R. A.; Nidy, E. G. *Ibid.* 1975, 40, 1680.
(18) Roberts, J. L., Jr.; Calderwood, T. S.; Sawyer, D. T. *J. Am. Chem. Soc.* 1983, 105, 7691.
(19) Roberts, J. L., Jr.; Sawyer, D. T. *J. Am. Chem. Soc.* 1981, 103, 712.

Scheme IV
Nucleophilic Addition/Displacement
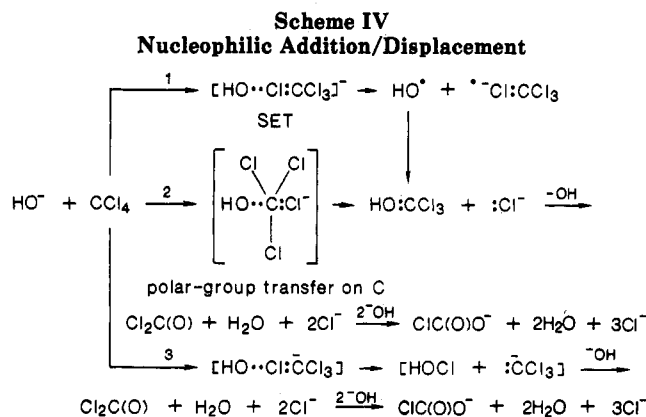
Scheme V
Polar-Group Transfer: ^-OH and $O_2^{\cdot-}$ Reactions with Esters
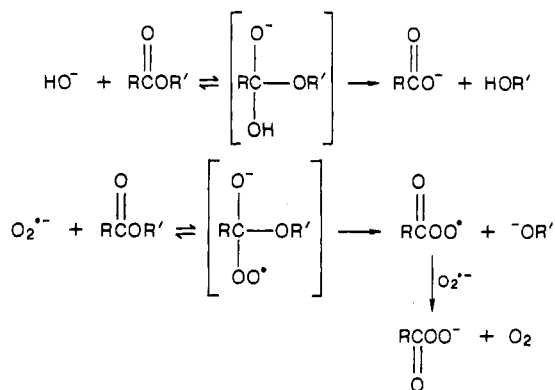
At least three alternatives must be considered to understand the nature of the primary reaction between ^-OH and CCl_4 (see Scheme IV): (1) a discrete SET reaction; (2) a polar-group-transfer on carbon, i.e., the formation of an HO–C bond with the concerted displacement of Cl^- (nucleophilic attack on carbon); (3) a polar-group-transfer on chlorine, i.e., the formation of an HO–Cl bond with the concerted displacement of Cl_3C^- (nucleophilic attack on chlorine).

The first alternative, a single-electron-transfer from ^-OH to CCl_4 is improbable because the reaction is about 1.5 V more endergonic than the analogous reaction with superoxide ion, yet proceeds at about 70% of the rate with $O_2^{\cdot-}$.[20] The rate of reaction of $O_2^{\cdot-}$ with polyhalogenated compounds $RCCl_3$ decreases about 10^5 per volt change in $E^{\circ\prime}$.[18] Although reaction 2 of Scheme IV would be expected to have a large reaction barrier due to the substantial atom motion required to enable a polar-group transfer on carbon, a recent study of the reaction of $O_2^{\cdot-}$ with CCl_4 indicates that $Cl_3COO^\cdot$ is the primary product (probably via reaction 1 of Scheme IV).[21] A third possibility for the reaction of HO^- may be a polar-group transfer on chlorine (reaction 3 of Scheme IV), which is analogous to a mechanism proposed for the reaction of CCl_4 with potassium *tert*-butoxide.[22] For the latter t-BuOCl is proposed as an intermediate to explain the isobutylene oxide product.
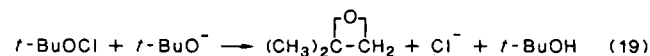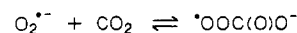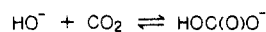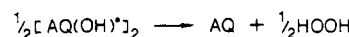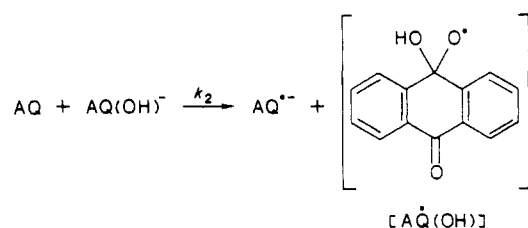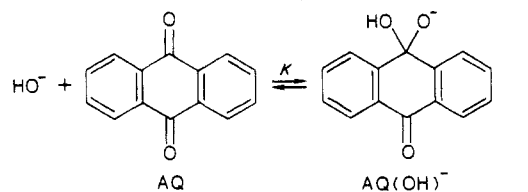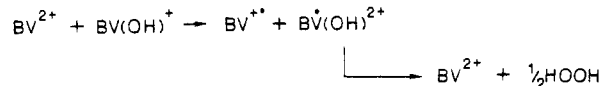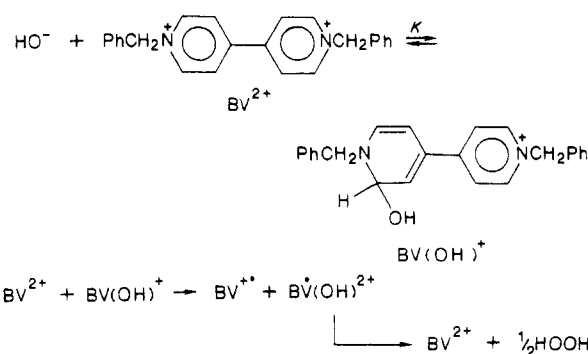
(20) Kane, C.; Roberts, J. L., Jr., unpublished data.
(21) Matsumoto, S.; Sugimoto, H.; Sawyer, D. T. *Chem. Res. Tox.* 1988, 1, 19.
(22) Meyers, C. Y.; Malte, A. M.; Matthews, W. S. *J. Am. Chem. Soc.* 1969, 91, 7510.

Scheme VI
Polar-Group Coupling

(a) $^-$OH and $O_2{}^{\cdot-}$ reaction with CO_2

$$HO^- + CO_2 \rightleftharpoons HOC(O)O^-$$

$$O_2{}^{\cdot-} + CO_2 \rightleftharpoons {}^\cdot OOC(O)O^-$$

(b) $^-$OH reaction with 9,10-anthraquinone

$$AQ + AQ(OH)^- \xrightarrow{k_2} AQ^{\cdot-} + [A\dot{Q}(OH)]$$

$$\tfrac{1}{2}[AQ(OH)^\cdot]_2 \longrightarrow AQ + \tfrac{1}{2}HOOH$$

(c) $^-$OH reaction with benzylviologen (BV^{2+})

$$BV^{2+} + BV(OH)^+ \longrightarrow BV^{\cdot+} + B\dot{V}(OH)^{2+}$$

$$\longrightarrow BV^{2+} + \tfrac{1}{2}HOOH$$

Finally, there is the possibility that the primary reaction involves another species entirely, such as an anion produced by deprotonating the solvent or from the addition of $^-$OH to a solvent molecule.

The reactions of $^-$OH and $O_2{}^{\cdot-}$ with the carbonyl group of esters[23,24] and quinones[25,26] share a common feature, the addition of the nucleophile to the carbonyl carbon. When a suitable leaving group is present, there is an essentially concerted elimination to give products, as shown in Scheme V.   The addition of $^-$OH to a carbonyl group in quinones, which have no leaving group, yields an adduct that may be sufficiently stable to characterize.[23]

Polar-Group-Coupling Reactions

Nucleophilic Addition Reactions. The most common addition reaction is to a carbonyl group without an adequate leaving group. Examples include the reaction of $^-$OH and $O_2{}^{\cdot-}$ with CO_2 and quinones.[25] A common feature of these reactions is the formation of an adduct that is sufficiently stable to be isolated or characterized (see Scheme VI).   The same orange species results from the reaction of solid tetramethylammonium superoxide with gaseous CO_2 and with neat

(23) Gibian, M. J.; Sawyer, D. T.; Ungermann, T.; Tangpoonpholvivat, R.; Morrison, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 640.
(24) Forrester, A. R.; Purushotham, V. *J. Chem. Soc., Chem. Commun.* **1984**, 1505.
(25) Roberts, J. L., Jr.; Sugimoto, H.; Barrette, W. C., Jr.; Sawyer, D. T. *J. Am. Chem. Soc.* **1985**, *107*, 4556.
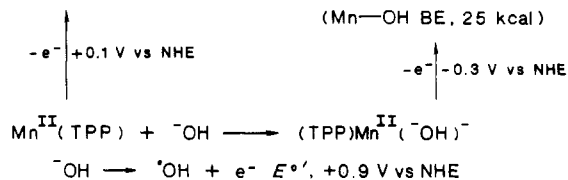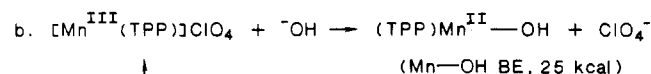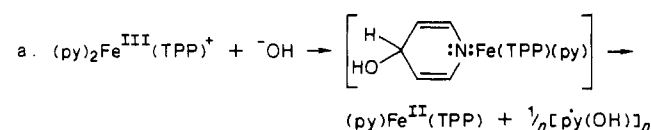(26) Bishop, C. A.; Tong, L. K. *Tetrahedron Lett.* **1964**, 3043.

Table IV
Equilibrium and Rate Constants for the Reactions of Quinones with Hydroxide Ion (See Scheme VI)[a]

quinone	K_1, M^{-1}	k_2, M^{-1} s^{-1}	adduct λ_{max}, nm	adduct log ϵ
p-benzoquinone monosulfonate	125		253	3.86
chloro-*p*-benzoquinone	364		267	4.00
2,5-dichloro-*p*-benzoquinone	1.7×10^3		250	4.00
trichlorohydroxy-*p*-benzoquinone	210		250	3.75
			365	3.70
tetrachloro-*p*-benzoquinone[b] (chloranil)	1×10^5		285	3.83
9,10-anthraquinone[c]	4.3×10^4	1.2	268	4.3
2-ethyl-9,10-anthraquinone[c]	4×10^4	4.2	268	

[a] Aqueous phosphate buffer, ionic strength 0.375, ref 26, unless otherwise indicated. [b] 50% aqueous ethanol, ref 26. [c] MeCN/tetra-*n*-butylammonium hydroxide, ref 25.

Scheme VII
Reductive Addition

$$(py)Fe^{II}(TPP) + \tfrac{1}{n}[p\dot{y}(OH)]_n$$

b. $[Mn^{III}(TPP)]ClO_4 + {}^-OH \longrightarrow (TPP)Mn^{II}{-}OH + ClO_4{}^-$

$$Mn^{II}(TPP) + {}^-OH \longrightarrow (TPP)Mn^{II}({}^-OH)^-$$

$${}^-OH \longrightarrow {}^\cdot OH + e^- \quad E^{\circ\prime}, +0.9 \text{ V vs NHE}$$

c. $(TPP)Fe^+ + {}^-OH \longrightarrow (TPP)Fe{-}OH$

$CCl_4{}^{27}$ and is believed to be the anion radical $^\cdot OOC(O)O^-$.[21]

The reaction of $^-$OH with 9,10-anthraquinone in MeCN produces an adduct stable at -20 °C,[25] which reacts further at room temperature to yield the semiquinone anion radical ($AQ^{\cdot-}$). The equilibrium constants for the formation of the adducts and the rate constants for the reaction of the adduct with a second quinone molecule are given in Table IV (see Scheme VI).

Reductive Addition Reactions. Several examples of reduction by HO$^-$ of transition-metal complexes are known (see Table III).[5,28-32] The reaction of Au$^+$ with HO$^-$ in MeCN is believed to be a prototype of reactions that involve a single-electron shift and the formation of a metal atom–hydroxyl radical bond.

$$HO:^- + Au^+ \rightarrow Au:OH(s) \qquad (20)$$
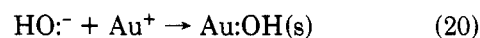
The $E^{\circ\prime}$ for the Au$^+$/Au redox couple in MeCN is $+1.58$ V vs NHE compared to $+0.9$ V for the HO$^\cdot$/HO$^-$ couple;[5,28] hence electron transfer is an exergonic process. Electrochemical oxidation of HO$^-$ at a gold electrode in MeCN occurs at -0.19 V vs NHE, which indicates an Au–OH bond energy of 26 kcal. [However, a Au–Au bond must be broken (54 kcal); this gives a value of 53 kcal ($26 + 54/2$) for the Au–OH bond.[4]]

(27) Roberts, J. L., Jr.; Calderwood, T. S.; Sawyer, D. T. *J. Am. Chem. Soc.* **1984**, *106*, 4667 and references therein.
(28) Goolsby, A. D.; Sawyer, D. T. *Anal. Chem.* **1968**, *40*, 1978.
(29) Hercules, D. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1966**, *88*, 4745.
(30) Srivatsa, G. S.; Sawyer, D. T. *Inorg. Chem.* **1985**, *24*, 1732.
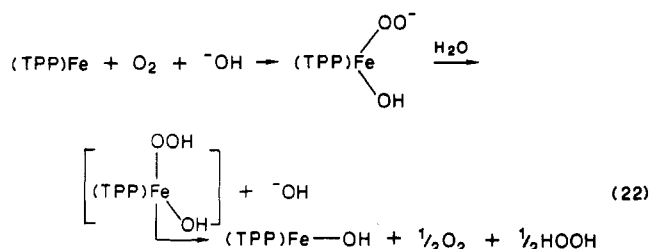(31) Tsang, P. K. S.; Sawyer, D. T., submitted to *J. Am. Chem. Soc.*
(32) Shin, K.; Kramer, S. K.; Goff, H. M. *Inorg. Chem.* **1987**, *26*, 4103.

The addition of ^-OH to manganese(III) complexes $[Mn^{III}(O_2\text{-bpy})_3]^{3+}$, $Mn^{III}(TPP)^+$ (TPP = dianion of tetraphenylporphyrin), $Mn^{III}(PA)_3$ (PA = picolinate anion), and $Mn^{III}(OAc)_3]$ in aprotic media results in the rapid precipitation of the same inorganic manganese oxide.[5]

$$Mn^{III}L_3 + 3^-OH \rightarrow 3L^- + Mn(OH)_3(s) + H_2O \quad (21)$$
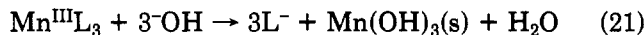
As in the case of Au^+ the higher valent state of manganese is reduced by electron transfer from three ^-OH ions. The resulting $^\bullet OH$ radicals are stabilized via three d^5sp-p covalent metal–oxygen bonds. Similar electron-transfer reductions by ^-OH have been reported from Ru(III) complexes[29] and for $(py)_2Fe^{III}(TPP)$-(ClO_4).[30] A mechanistic pathway for the latter process is outlined in Scheme VII, as is the reduction of $Mn^{III}(TPP)(ClO_4)$ by ^-OH.[5] The direct reduction of $[(TPP)Fe^{III}]X$ via addition of ^-OH has been observed via electrochemical measurements[31] and an NMR titration (Scheme VII).[32]

Another example of reductive addition by ^-OH is its termolecular reaction with reduced Fe(TPP) in the presence of dioxygen.[31]

$$\left[\begin{array}{c} OOH \\ | \\ (TPP)Fe \\ \diagdown_{OH} \end{array} \right] + {}^-OH \quad (22)$$

$$(TPP)Fe—OH + \tfrac{1}{2}O_2 + \tfrac{1}{2}HOOH$$

The net effect is the reduction of O_2 to bound superoxide ion, which hydrolyzes to bound $HOO^\bullet$, which dissociates from the iron center and disproportionates to HOOH and O_2.

Single-Electron-Transfer (SET) Reactions

The most striking and unexpected reactions of HO^- are those that produce anion radicals when HO^- is added to solutions of aromatic ketones, quinones, paraquats, and strong acceptors such as tetracyanoethene.[16] If the primary reaction is a SET reaction, a free-radical pair will be produced.

$$HO:{}^- + X:Y \rightarrow HO^\bullet + X:Y^{\bullet-} \quad (23)$$
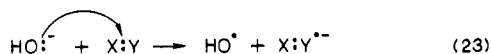
Because $HO^\bullet$ is a strong oxidant (although about 1 V weaker in MeCN than in water), a single-electron transfer would be greater than 1 V endergonic for quinones, paraquats, and ketones. All of these compounds, unless substituted with electron-withdrawing groups, are reduced at potentials less negative than -0.3 V vs NHE in MeCN, compared to $+0.9$ V for the $HO^\bullet/HO^-$ redox couple. Hence, the reactions of quinones, paraquats, and ketones with ^-OH are unlikely examples of the SET process. Only synchronous coupling of the electron transfer to a chemical reaction that results in covalent bond formation of the $HO^\bullet$ can account for the spontaneous reactivity. Although the coupling of two $HO^\bullet$ to form HOOH is one possibility, a more likely primary step for reactants is attack by ^-OH of an unsaturated center (aromatic or carbonyl carbon compound), or in the case of the paraquats, a dequaternization reaction initiated by addition. The observed free radicals are then produced in subsequent

Scheme VIII
Hydroxyl Radical Reaction Patterns

A. H-Atom Abstraction from Aliphatic Compounds
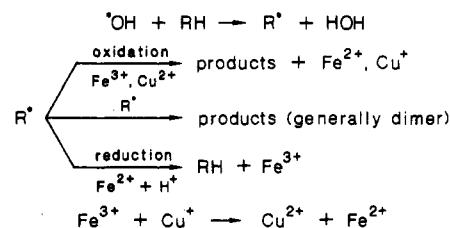
B. Hydroxyl Radical Addition to Aromatic Compounds
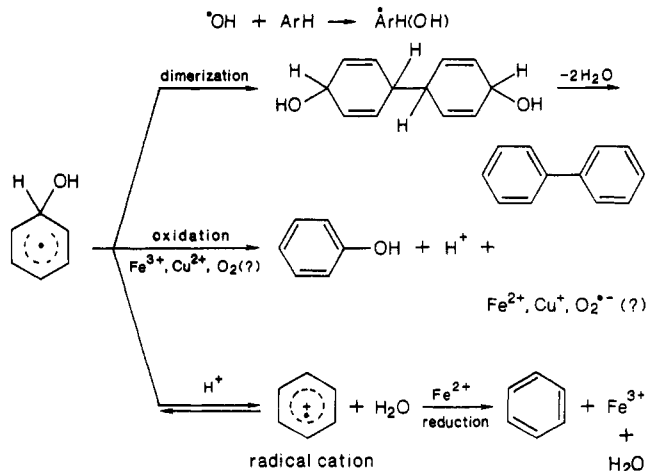
reactions that involve the intermediates from the primary step. Thus, the production of a free radical is not adequate evidence that the primary step is a SET reaction.

In aprotic solvents ^-OH reacts with elemental sulfur (S_8) via a net SET process to give the trisulfide anion radical $(S_3^{\bullet-})$ and HOOH.[33]

$$3S_8 + {}^-OH \rightarrow 8S_3^{\bullet-} + 4HOOH \quad (24)$$
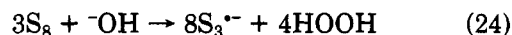
Perhaps this is the most compelling example that ^-OH represents a stabilized electron and can affect the electron-transfer reduction of a nonmetal to give an anion radical.

Some of the reactions of ^-OH with quinones are accelerated by light ($\lambda < 500$ nm); the reaction rates are proportional to the light intensity, the concentration of quinone, and the concentration of hydroxide.[16] These reactions appear to involve direct electron transfer from a hydroxide ion to an excited anthraquinone molecule. The endergonic barrier of the ground-state molecule is removed via the orbital vacancy that is created by photoexcitation, which corresponds to an energy state of greater electron affinity. The effect of light in the reactions of ^-OH with electron-acceptor molecules that absorb in the UV–visible may be more general than heretofore realized.

Any bona fide example of a primary SET step must involve an electron acceptor with a positive redox potential so that the electron transfer is not strongly endergonic. Two molecules that react with ^-OH fulfill this condition: tetracyanoethene and 2,2,6,6-tetramethylpiperidine-1-oxonium (TEMPO$^+$, Table III). What is the fate of an $HO^\bullet$ radical that is produced in a SET reaction? Pulse radiolysis studies in aqueous solution confirm that it is highly reactive[10] and that it rapidly

(33) Hojo, M.; Sawyer, D. T., submitted to *Inorg. Chem.*

disappears via the paths outlined in Scheme VIII to give various products (these provide circumstantial evidence for its production).

The production of a stoichiometric quantity of hydrogen peroxide (in an O_2-free system) provides strong evidence for the formation of HO• radical. Yields of 90% are obtained in pH 9–11 aqueous $NaHCO_3/Na_2CO_3$ buffer on the basis of iodometric assay of the aqueous solution, with quantitative recovery of the TEMPO free radical product by ether extraction of the aqueous layer.[34] The mass spectrum of the reaction products includes a peak at mass 34.

Although this reaction appears to be a clear-cut example of a SET reaction, several presumptions are necessary. First the bimolecular reaction to form hydrogen peroxide is assumed to be faster than reaction of HO• either with CO_3^{2-} or with TEMPO radical (the latter is produced with HO• in the solvent cage). Second, formation of HOOH is assumed to be solely via •OH coupling (it also can be formed from secondary reactions, e.g., from peroxy dicarbonates).[27] Because iodometry is a nonselective method that measures other peroxides as well as hydrogen peroxide, the mass-34 peak is the only definitive evidence for HOOH.

Summary

1. Solvation of ⁻OH affects to a major degree the thermodynamics and kinetics for its reaction with electron-acceptor molecules. Solvation energies determine the ionization energy of ⁻OH (and its redox potential as an electron donor) and the electron affinity of the electron-acceptor molecule.

2. All reactions of ⁻OH (and of nucleophiles) can be classified as a single-electron shift that leads to a polar pathway or an SET pathway.

3. The barrier to reaction, which includes kinetic and thermodynamic components, is controlled by the solvation energies of the reactants and products and their redox potentials and bond energies. The electron-transfer propensity of ⁻OH increases in proportion to the covalent bond energy of the product–OH adduct.

4. Most of the known reactions of ⁻OH that produce free radicals probably do not involve a direct single-electron transfer (SET) from ⁻OH in the primary step because an SET primary step is usually highly endothermic; the primary step more often is an approximately thermoneutral polar reaction (polar-group transfer or polar-group coupling), with secondary reactions producing free radicals that are coupled to form stable M–OH bonds (M is a molecule or metal atom with an unpaired electron).

(34) Endo, T.; Miyazawa, T.; Shiihasi, S.; Okawara, M. *J. Am. Chem. Soc.* 1984, *106*, 3877.