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One-Electron Oxidation of Odd-Valent Metal Ions in Solution

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The fast-reaction technique of pulse radiolysis and kinetic absorption spectrophotometry was used to generate odd-valent metal ions in neutral aqueous solution, and study their one-electron oxidation reactions. Using the sulfate and perchlorate salts, the M^{2+} ions were reduced to the M^+ ions by e_{aq}^- . The Zn^+ , Co^+ , Cd^+ , Pb^+ , Ni^+ , as well as Cr^{2+} and Tl^0 , odd-valent metal ions were produced. The one-electron oxidation of these odd-valent metal ions was studied in the presence of various electron acceptors A (including phenones, dyes, and quinones) whose two-electron redox potentials E^{01} (V, at pH 7.0, 25°) are known. The percentage efficiency of the electron transfer reaction $M^+ + A \rightarrow M^{2+} + \cdot A^-$ was found to be dependent upon the E^{01} values of the acceptors. Titration-type curves are obtained, and from the midpoint (50% electron transfer) kinetic potentials for the $M^+|M^{2+}$ redox couples were derived. These potentials are not the thermodynamic values since the electron transfer processes followed were found to be irreversible, under the experimental conditions used. The results show that the reducing power of the odd-valent metal ions decreases in the order $Zn^+ \geq Co^+ \geq Cd^+ > Tl^0 > Pb^+ > Ni^+ > Cr^{2+}$.

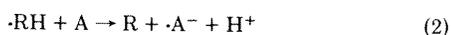
Introduction

Most divalent transition metal ions react with e_{aq}^- with high rate constants¹ in aqueous solution. The products of the reaction with e_{aq}^- are the monovalent ions in their ground states (reaction 1). The formation of Co^+ , Zn^+ ,



Cd^+ , and Ni^+ have been shown based on their uv absorption spectra.² The ESR of some of these odd-valent metal ions were also observed in frozen solutions.³ These reduced species have been found to react with various oxidants, including O_2 , N_2O , H_2O_2 , NO_2^- , NO_3^- , alkyl halides, etc. (see ref 1, p 122). It was shown⁴ that Zn^+ is more reactive than Cd^+ , and that both species are much more reactive than Ni^+ . Explanations for some of these observations have been suggested,¹⁻⁴ based on the configuration of the metal ions and the type of electron transfer (inner sphere vs. outer sphere) mechanism.

We have recently developed a method,⁵ using the pulse radiolysis technique, for determining the kinetic (not thermodynamic) potentials of free radicals in aqueous solutions. This method is based on the one-electron redox properties of the free radicals, $\cdot RH$, in the presence of electron acceptors, A, whose two-electron redox potentials (E^{01} , pH 7.0, ~25°) in water are known:



The rate constants of reaction 2 and the efficiencies of for-

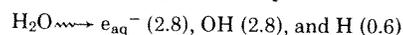
mation of $\cdot A^-$ were shown to be dependent on the E^{01} values of the acceptors used. A plot of the percentage efficiency for electron transfer vs. E^{01} of the acceptors gave "titration-type" curves, and from the midpoint (50%) the kinetic potentials of the radicals, E_k^{01} , were derived.

This method has been used to obtain the kinetic potentials of odd-valent metal ions in water. The results obtained for the following redox couples are presented below: $Zn^+|Zn^{2+}$, $Co^+|Co^{2+}$, $Cd^+|Cd^{2+}$, $Tl^0|Tl^+$, $Pb^+|Pb^{2+}$, $Ni^+|Ni^{2+}$, and $Cr^{2+}|Cr^{3+}$.

Experimental Section

The pulse radiolysis and kinetic absorption spectrophotometry experimental set-up used have been described.^{6,7} Single pulses of ~2.3 MeV electrons and ~30-nsec duration were provided from a Febetron 705 machine (Field Emission Corp.).

The radiation chemistry of water produces



where the numbers in parentheses are the G values (number of free radicals formed per 100 eV of energy absorbed by the water). The experimental condition used to generate the odd-valent metal ions in water was a one-electron reduction of Zn^{2+} , Co^{2+} , Cd^{2+} , Tl^+ , Pb^{2+} , Ni^{2+} , and Cr^{3+} salts by e_{aq}^- , reaction 1. These experiments were carried out using 5 mM concentration of the salts in the presence of ~1.0 M *tert*-butyl alcohol to scavenge⁶ the OH radicals.

The sulfate salts were used for all metal ions, except for lead and chromic when the perchlorate salts were used.

The experimental conditions used to study the one-electron oxidation of these odd-valent metal ions in the presence of electron acceptors were described in detail.⁵ The concentration of the acceptors A was $5 \times 10^{-5} M$, except for dyes when $2.0\text{--}2.5 \times 10^{-5} M$ concentrations were used. Under all conditions, all the e_{aq}^- reacted with the metal ions, none with the acceptors, and the $[A]/[M^+] \geq 15$. Relatively low concentrations of e_{aq}^- were used, $\sim 1\text{--}2 \mu M$. Table I lists the acceptors employed in this work. Their redox potentials were obtained from the literature,⁹ and the values are for two-electron changes.

The 100% efficiency level for formation of $\cdot A^-$ radicals, or for "bleaching" of the dyes, was established in each case from the reaction of the acceptors with e_{aq}^- in the absence of the metal ions (eq 3). The wavelengths used to monitor



the formation of $\cdot A^-$, or the bleaching of the dye, are given in ref 5 and 8.

Chemicals were the highest research grade commercially available and were purchased from Baker and Adamson, J. T. Baker, Mallinckrodt, Aldrich, and Eastman Chemicals. Solutions were buffered at pH 7.0 with $\sim 1 mM$ phosphates.

Results and Discussion

All the metal ions examined react with e_{aq}^- at diffusion-controlled rates¹ in water at pH 7.0. Under the experimental conditions used, the odd-valent metal ions are produced in $\leq 10^{-8}$ sec. The nature of the aquo-metal complex of these species present in sulfate (or perchlorate) solutions at pH 7.0 are not known or assumed in this work. For convenience, the odd-valent ions are represented as M^+ (for Zn^+ , Co^+ , Cd^+ , Pb^+ , and Ni^+), M^{2+} (for Cr^{2+}), and M^0 (for Tl^0). In the case of Tl^0 , the actual species present¹⁰ in these solutions may be Tl_2^+ , produced from the reaction $Tl^0 + Tl^+ \rightarrow Tl_2^+$.

The lifetimes and decay characteristics of these odd-valent metal ions are known¹⁻⁴ only in general terms. It was assumed (as was found to be the case) that their reaction with the acceptors would occur in a time scale significantly shorter than their natural lifetimes, under the experimental conditions used.

Oxidation of Zn^+ , Co^+ , and Cd^+ Ions. The reaction of, for example, Co^+ with menaquinone (MQ) has already been shown¹¹ to form the $MQ\cdot^-$ radical anion, whose transient spectrum and extinction coefficient is in complete agreement with literature data on the spectral properties of $MQ\cdot^-$. The dependence of the percentage efficiencies for the one-electron oxidation of these ions, reaction 4, upon



the redox potential of the acceptors used are shown in Figure 1. A rapid change can be observed with acceptors whose E^{01} values are in the range -1.1 to -1.0 V. Small, but experimentally distinguishable, differences were observed for Zn^+ , Co^+ , and Cd^+ .

The presence of the β -hydroxyl alkyl radical produced from *tert*-butyl alcohol (present in solution to scavenge the OH radicals) was found not to interfere with the results observed. This was established as follows: (a) the percentage of $\cdot BP^-$ (BP = benzophenone) formed from the reaction of Co^+ and Zn^+ with BP was 80–84%, in solutions containing 5 mM $CoSO_4$ or $ZnSO_4$, pH 7.0, in the presence of either 1.0 M *t*-BuOH, 1.0 M *i*-PrOH, or 1.0 M HCO_2^- used to sca-

TABLE I: List of Electron Acceptors Used

	E^{01} , V ^a
1. 4,4'-Dimethoxybenzophenone	-1.120
2. <i>p</i> -Chlorobenzophenone	-1.050
3. Benzophenone	-1.00
4. <i>p</i> -Cyanobenzophenone	-0.80
5. 3-Benzoylpyridine	-0.75
6. Fluorenone	-0.68
7. Rhodamine B	-0.54
8. Eosin Y	-0.50
9. Crystal Violet	-0.357
10. Safranin T	-0.289
11. Phenosafranin	-0.254
12. Anthraquinone 2,6-disulfonate	-0.184
13. Indigodisulfonate	-0.125
14. Menaquinone	+0.002

^a See ref 9, 5, and 8.

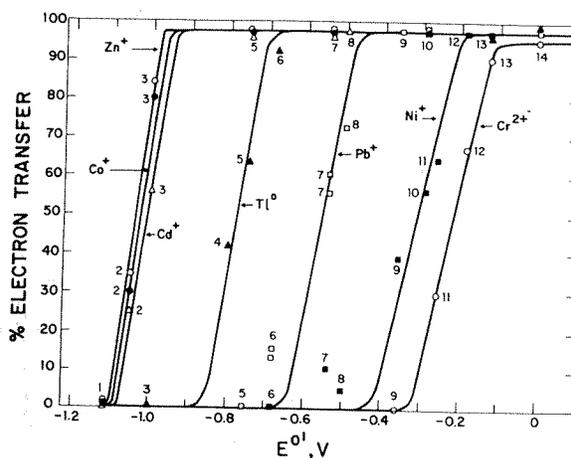
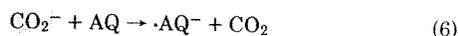
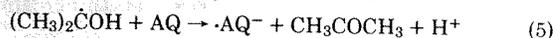


Figure 1. Dependence of the percentage efficiency for the one-electron oxidation of odd-valent metal ions upon the redox potential (E^{01} , V) at pH 7.0 and $\sim 25^\circ$ of the electron acceptors A. Experiments carried out in aqueous solutions using $5 \times 10^{-3} M$ of the metal sulfates (except for Pb^{2+} and Cr^{3+} perchlorates) at pH 7.0, in the presence of $2.5\text{--}5 \times 10^{-5} M$ concentration of the acceptors. See text for further experimental details and Table I for the list of electron acceptors used.

venge the OH radicals. The *t*-BuOH radical and the $(CH_3)_2\dot{C}OH$ and $CO_2\cdot^-$ radicals formed did not react with Zn^+ or Co^+ , Zn^{2+} or Co^{2+} , or with BP . The latter was already established;⁵ (b) in 5 mM solutions of $NiSO_4$, $5 \times 10^{-5} M$ anthraquinone 2,6-disulfonate (AQ), pH 7.0, 1 atm of argon, $\sim 100\%$ formation of $\cdot AQ^-$ was found in 1.0 M *t*-BuOH (Figure 1). An almost doubling in the yield of $\cdot AQ^-$ was observed in the presence of 1.0 M *i*-PrOH or 1.0 M HCO_2^- . This is explained on the basis of reactions 5 and 6. These reactions have already been established.⁵



Under the experimental conditions used, reaction 4 was found to be irreversible. This was concluded on the basis of an absence of a dependence on the formation (both rate of formation and efficiency) of $\cdot A^-$ upon $[M^{2+}]$, over the range up to $5 \times 10^{-2} M$. The decay kinetics of $\cdot A^-$ was also not affected by the concentration of M^{2+} ions. Hence thermodynamic redox potentials cannot be derived from these results. The potentials are referred to as kinetic potentials.^{5b}

TABLE II: Kinetic Potential of Odd-Valent Metal Ions in Water at pH 7.0, 25°

System	Redox couple ^a	E_k^{01} , V ^b
ZnSO ₄	Zn ⁺ Zn ²⁺	-1.04
CoSO ₄	Co ⁺ Co ²⁺	-1.02
CdSO ₄	Cd ⁺ Cd ²⁺	-1.01
Tl ₂ SO ₄	Tl ⁰⁺ Tl ⁺	-0.78
Pb(ClO ₄) ₂	Pb ⁺ Pb ²⁺	-0.56
NiSO ₄	Ni ⁺ Ni ²⁺	-0.31
Cr(ClO ₄) ₃	Cr ²⁺ Cr ³⁺	-0.21

^a The redox couple studied is for the one-electron oxidation of the lower valent ion to the higher valent ion (see text). ^b Values are derived from the midpoints (50% electron transfer) of the curves in Figure 1; values are good to ± 0.03 V; the signs are given for the reduction process, in agreement with convention (i.e., the kinetic oxidation potential for the Zn⁺|Zn²⁺ couple is +1.04 V).

From the midpoint (50% electron transfer) of the curves given in Figure 1, the kinetic potentials, E_k^{01} , of these odd-valent metal ions can be derived and are given in Table II. The results indicate that these monovalent ions are powerful reducing agents, capable of reducing molecules with E^{01} values greater than ~ -1.0 V. A recent study^{12a} of Co(I) complexes containing unsaturated macrocyclic ligands gave a $E_k^{01} = -0.88$ V for the Co^I(4,11-diene-N₄) species.

The thermodynamic redox potentials for the Zn⁺|Zn²⁺ and Cd⁺|Cd²⁺ couples have recently been calculated.^{12b} Values of -2.0 ± 0.4 and -1.8 ± 0.4 V, respectively, were derived. On the basis of Marcus' theory¹³ for electron transfer reactions, the redox potentials for the couples Zn⁺|Zn²⁺ and Cd⁺|Cd²⁺ were estimated^{14,12b} as -1.0 and ≤ -0.5 V, respectively. The E_k^{01} values of ~ -1.0 V for these couples appear to be closer to the E^{01} values calculated on the basis of Marcus' theory. It should be pointed out, however, that while thermodynamic redox potentials provide information as to whether a reaction is energetically feasible, the kinetic potentials provide information on the occurrence and rate constants of the reaction. Neither method, however, provides any information on the mechanism of the electron transfer reaction.

Oxidation of Pb⁺ and Ni⁺ Ions. The results obtained are presented in Figure 1 and the E_k^{01} values derived are given in Table II.

Ionization constant values ranging from 7.1 to 8.8 have been obtained¹⁵ for the hydrolysis of Pb²⁺ ions. Hence there is uncertainty on the nature of the Pb⁺ species present at pH 7.0. A E_k^{01} value of -0.57 V is obtained for the Pb⁺|Pb²⁺ couple making this metal ion a poorer reducing agent compared to Zn⁺, Co⁺, and Cd⁺.

Ni⁺ is an even poorer reducing agent, with E_k^{01} of -0.31 V. E^{01} value of -0.7 ± 0.4 V have been derived^{12b} for the Ni⁺|Ni²⁺ couple, while the value estimated from thermodynamic data¹⁶ is -2.7 V. A value of -0.7 V was derived¹⁴ based on Marcus' theory.

The Ni(I) complexes of unsaturated macrocyclic ligands have been studied¹⁷ and their kinetic potentials determined.

Oxidation of Cr²⁺ Ions. The Cr²⁺ ions were produced from the reaction of e_{aq}⁻ with chromic perchlorate at pH 7.0. The oxidation of Cr²⁺ to Cr³⁺ was found to have a E_k^{01} value of -0.21 V; see Figure 1 and Table II.

In perchloric acid solutions at pH 3.4, the one-electron oxidation of the Cr²⁺ species to Cr³⁺ occurred at a much higher (i.e., more positive) potential. A E_k^{01} value of

TABLE III: Reaction Rate Constants of Odd-Valent Metal Ions with Electron Acceptors in Aqueous Solution, pH 7.0

System	Odd-valent ion	Acceptor ^a	k , M ⁻¹ sec ^{-1b}
ZnSO ₄	Zn ⁺	<i>p</i> -Benzoquinone (+0.293)	4.8×10^9
		Menaquinone (+0.002)	3.8×10^9
		Benzophenone (-1.00)	2.5×10^9
CoSO ₄	Co ⁺	<i>p</i> -Benzoquinone (+0.293)	4.8×10^9
		Menaquinone (+0.002)	4.0×10^9
		Benzophenone (-1.00)	2.5×10^9
CdSO ₄	Cd ⁺	<i>p</i> -Benzoquinone (+0.293)	4.4×10^9
		Menaquinone (+0.002)	4.6×10^9
		Benzophenone (-1.00)	1.0×10^9
Tl ₂ SO ₄	Tl ⁰⁺	<i>p</i> -Benzoquinone (+0.293)	2.8×10^9
Pb(ClO ₄) ₂	Pb ⁺	Menaquinone (+0.002)	3.7×10^9
NiSO ₄	Ni ⁺	Menaquinone (+0.002)	2.4×10^9
Cr(ClO ₄) ₃	Cr ²⁺	<i>p</i> -Benzoquinone (+0.293)	3.5×10^9
		Anthraquinone 2,6-disulfonate (-0.184)	2.8×10^9

^a Numbers in parentheses are the redox potentials of the acceptors. ^b Determined by monitoring the formation kinetics of $\cdot A^-$ radicals at appropriate wavelengths, $M^+ + A \rightarrow M^{2+} + \cdot A^-$ (see text).

$\sim +0.35$ V was found, making the Cr²⁺ species at pH 3.0 a poorer reducing agent than at pH 7.0. A pK_a for the hydrolysis of Cr³⁺ of ~ 4.0 has been reported.¹⁵ The redox potential for the Cr³⁺ couple in 1.5×10^{-3} M H₂SO₄ was reported¹⁸ to be -0.41 V. This is a clear example where the pH and the nature of the aquo-metal complex ion can considerably affect the redox properties of the ions.

Oxidation of Tl⁰. As mentioned above, the form and nature of the species present at pH 7.0 are uncertain. Figure 1 and Table II show the results obtained.

The one-electron of the "Tl⁰" species shows this ion to be a relatively strong reducing agent, with $E_k^{01} = -0.77$ V. The redox potential for the Tl⁺|Tl⁰ couple is reported¹⁸ to be -0.336 V. This is considerably different from the E_k^{01} value found for the reverse process. Among other reasons which may account for this difference is the nature of the "Tl⁰" species present in solutions which is oxidized to Tl⁺.

Oxidation of Ag⁰ and Cu⁺ Ions. Some preliminary experiments with Ag(SO₄)₂ and CuSO₄ were carried out at pH 3.0. Considerable irreproducibility was observed with these ions at pH 7.0 and also at pH 3.0.

It appears that the "Ag⁰" species present at pH 3.0 is a poor reducing agent with $E_k^{01} \sim +0.5$ V for the Ag⁰|Ag⁺ couple. Similarly, the oxidation of "Cu⁺" at pH 3.0 is equally difficult, with $E_k^{01} > +0.4$ V for the Cu⁺|Cu²⁺ couple. Due to the observed irreproducibility of these systems, the E_k^{01} values given above are probably not significant.

Conclusions

The kinetic potentials for the Zn⁺|Zn²⁺, Co⁺|Co²⁺, Cd⁺|Cd²⁺, Pb⁺|Pb²⁺, Ni⁺|Ni²⁺, Cr²⁺|Cr³⁺, and Tl⁰|Tl⁺ couples in water at pH 7.0 were derived. For most of these one-electron redox couples, no calculated thermodynamic redox potentials are known. The results obtained here appear to be relevant to the chemical reactivity of these odd-valent metal ions in water.

The reaction rate constants of these ions with a number of the acceptors used are given in Table III. These values

are close to diffusion-controlled rates for acceptors which have higher (more positive) potentials than the oxidation potentials of the $M^+|M^{2+}$ couples.

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