solvent. Solutes, such as ethanol and methanol, which are apparently inert toward solvated electrons are often used in relatively high concentrations to assist in elucidating radiation chemical processes occurring immediately after the deposition of energy in aqueous solutions. It is now clear from our findings that reactions between the radiation products of these solutes (i.e., the aliphatic free radicals) and the solvated electrons should always be considered for such systems, particularly since it is in the spur regions where early processes occur. In addition, it is also to be expected that isotope exchange reactions may take place in more complex molecules, for example, carbohydrates. If such exchange occurs at a chiral center, then, by analogy with our observations with cyclohexane-1,2-diols, the reaction may lead not only to the parent compound but also to an inversion product. Radiation-induced hydrogen isotope exchange reactions may therefore deserve consideration not only in an analysis of the radiation chemistry of aqueous solutions and of the chemistry of simple free radicals but also in a discussion of radiobiological processes.

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Complexes of Cations in Unstable Oxidation States in Aqueous Solutions as Studied by Pulse Radiolysis

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The radiolysis of water has been the subject of many recent studies. The detailed mechanisms of the primary steps leading to the decomposition of water by ionizing radiation have not been fully elucidated. However the results clearly indicate that the primary processes occurring during the radiolysis of water and dilute aqueous solutions may be summarized by eq 1.[1] These

$$\mathrm{H_2O} \xrightarrow{\gamma,\, e^-} e_{aq}^-, \cdot\mathrm{H}, \cdot\mathrm{OH}, \mathrm{H_2}, \mathrm{H_2O_2}, \mathrm{H_3O^+} \tag{1}$$

products are formed in a homogeneous solution within less than 100 ns after the radiation is absorbed. The yields of these primary products in dilute aqueous solutions are $G_{e_{aq}^-} = 2.65$, $G_{\mathrm{OH}} = 2.65$, $G_{\mathrm{H}} = 0.60$, $G_{\mathrm{H_2}} = 0.45$, and $G_{\mathrm{H_2O_2}} = 0.75$[1] (where G is the number of product molecules formed per 100 eV absorbed by the solution).

The radicals e_{aq}^-, OH, and H are strong single-electron redox reagents. The use of these reagents is complicated by the fact that nearly equal amounts of very strong reducing (e_{aq}^-, H·) and oxidizing (·OH, H·) reagents are formed simultaneously. However, work under strong oxidizing or reducing conditions is made possible by applying one of the following reactions:

$$e_{aq}^- + \mathrm{N_2O} \rightarrow \mathrm{N_2} + \mathrm{O^-} \qquad k_2 = 5.6 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}\ {}^{2} \tag{2}$$

followed by

$$\mathrm{O^-} + \mathrm{H_2O} \rightleftarrows \mathrm{OH} + \mathrm{OH^-} \qquad \mathrm{p}K_2 = 11.9 \pm 0.2\ {}^{3} \tag{2a}$$

$$e_{aq}^- + \mathrm{H_3O^+} \rightarrow \mathrm{H} \qquad k_3 = 2.3 \times 10^{10}\ \mathrm{M^{-1}\,s^{-1}}\ {}^{4} \tag{3}$$

$$\mathrm{OH/H} + \mathrm{RH_2} \rightarrow \cdot\mathrm{RH} + \mathrm{H_2O/H_2}\ {}^{5,6} \tag{4}$$

(where RH is a saturated aliphatic compound and the radical ·RH is a reducing agent, an oxidizing agent, or unreactive, depending on the nature of $\mathrm{RH_2}$ and the system studied; see below).

$$\mathrm{OH} + \mathrm{H_2} \rightarrow \mathrm{H} + \mathrm{H_2O} \qquad k_5 = 6 \times 10^7\ \mathrm{M^{-1}\,s^{-1}}\ {}^{7} \tag{5}$$

$$\mathrm{H} + \mathrm{OH^-} \rightarrow e_{aq}^- \qquad k_6 = 2.3 \times 10^7\ \mathrm{M^{-1}\,s^{-1}}\ {}^{8} \tag{6}$$

Furthermore, a series of other strong single-electron redox reagents can be produced by adding appropriate solutes, e.g., $\mathrm{I_2^-}$,[9,10] $\mathrm{Br_2^-}$,[9,11] $\mathrm{(NCS)_2^-}$[12] in solutions containing $\mathrm{N_2O}$ and $\mathrm{I^-}$, $\mathrm{Br^-}$, or $\mathrm{NCS^-}$, respectively; $\mathrm{Cl_2^-}$ in acidic solutions containing $\mathrm{Cl^-}$;[9,13] $\mathrm{O_2^-}$ or $\mathrm{HO_2}$ de-

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pending on the pH in solutions containing O_2 and HCO_2^-;[14–16] CO_2^- in solutions containing N_2O and HCO_2^-;[17,18] O_3^- in alkaline solutions containing N_2O and O_2;[19] $R_1R_2\dot{C}OH$ in solutions containing R_1R_2CHOH,[18,20] etc.

Experimentally the radiation source is usually a linear accelerator or a Van de Graff producing electrons with an energy of 2–20 MeV.[1] The pulse length is usually between 10 ns and 2 μs with a current of 50 mAp–2 A. (In some setups shorter pulses, down to 10 ps, and larger currents are available.) The solutions saturated with the required gas are placed in a quarz cell in front of the electron beam. The penetration range of electrons in water is 0.5 cm/MeV.[1] In most setups solutions containing up to 5×10^{-5} M of the free radicals can be formed within less than 1 μs. The kinetics of reaction of the radicals may be followed by spectrophotometric,[1] EPR,[21] conductance,[22] and polarographic[23,24] techniques.

The pulse radiolytic technique has two major advantages for studying the properties of complexes in unstable oxidation states in aqueous solutions: (a) the technique enables, within very short time, the formation of highly unstable intermediates in concentrations which can be followed by physical methods; (b) the technique produces one-electron redox reagents, thus ensuring that the first products observed are the products of one-electron redox processes, even in systems which prefer two-electron reactions (e.g., Tl(II), Pt(III), Au(II), and Cu(I) are formed in the reduction of Tl(III), Pt(IV), Au(III), and Cu(II) or in the oxidation of Tl(I), Pt(II), and Au(I), respectively). The major disadvantage of the technique is that, due to the very high reactivity of the primary free radicals, they also often react with the products. Therefore, only experiments with very small conversions of the starting materials are meaningful; sometimes it is not possible to obtain a quantitative analysis of the final products. Thus the mechanistic arguments are often based on kinetic data only. A second disadvantage is that in complicated systems, e.g., complexes with large organic ligands, the highly reactive primary free radicals might attack the complex at several sites, producing several intermediates. Thus complex kinetics are expected. This difficulty can often be circumvented by using secondary, less reactive, free radicals as redox reagents. However, as most of the free radicals used disappear in the absence of additives via second-order processes, approaching the diffusion-controlled limit,[10–13,17,20] only their reactions with complexes having specific rates $>1 \times 10^6$ M^{-1} s^{-1} can be studied.

Thus far the main application of the pulse-radiolytic technique to inorganic chemistry has been the study of complexes in unstable oxidation states. The results may be divided into three major groups:

Complexes in Low Oxidation States

The redox potential of e_{aq}^- ($\epsilon^0 = 2.77$ V)[25] is sufficient to reduce most cations in their lowest common oxidation state. Indeed, it was found that e_{aq}^- reacts with complexes of all cations, alkaline and alkaline-earth cations[26] excepted. (No data are available on the reactivity of V^{2+}, Mo^{2+}, Bi^{3+}, Cu^+, Eu^{2+}, and any Ge, Nb, Hf, Ta, W, and Re ions.) However, it was found that e_{aq}^- is unreactive, $k_{e_{aq}^- + \text{complex}} < 1 \times 10^6$ M^{-1} s^{-1}, toward some complexes, e.g., $[Fe(CN)_6]^{4-}$,[27] $[Ru(CN)_6]^{4-}$,[27] $LaEDTA^-$,[28] $ZnEDTA^{2-}$,[28] probably due to kinetic factors. It should be pointed out that the primary product of reaction of a reducing radical (e.g., e_{aq}^-, H, $\cdot CH_2OH$) with a complex is not necessarily the one step lower valent complex. The radicals might also react with the ligand (e.g., $e_{aq}^- + [(NH_3)_5Co^{III}{-}^{-}O_2CC_6H_4NO_2] \rightarrow [(NH_3)_5Co^{III}{-}^{-}O_2C\dot{C}_6H_4NO_2^-])$.[29] Thus it seems reasonable that hydrogen atoms do not reduce $[Fe(CN)_6]^{4-}$ forming $[Fe(I)(CN)_6^{5-}]$, as has been suggested,[30] but attack one of the cyanide groups. Evidently, such processes are probable only for ligands liable to be attacked by free radicals and not for simple ligands like H_2O, OH^-, NH_3, etc.

It is of interest to note that most of the low valent cations do not decompose by reacting with H_2O or H_3O^+. The reason for this seems to be that the reactions

$$M_{aq}^{(n-1)+} + H_2O(\text{or } H_3O^+) \rightarrow M^{n+} + H_{aq} + OH^-(\text{or } H_2O) \quad (7)$$

are endothermic, in view of the redox potential of the couple H_{aq}/H_3O^+ for which $E^0 = 2.28$ V.[31] Thus only reactions of the type

$$M(H_2O)_l^{(n-1)+} \rightarrow M(H_2O)_{l-2}(OH)_2^{(n-1)+} + H_2 \quad (8)$$

or

$$M(H_2O)_l^{(n-1)+} \rightarrow M(H_2O)_{l-1}O^{(n-1)+} + H_2 \quad (9)$$

or

$$M(H_2O)_l^{(n-1)+} + H_3O^+ \rightarrow M(H_2O)_{l-1}H^{n+} + 2H_2O \quad (10)$$

are plausible. Such reactions might be expected only for cations for which the $M^{(n+1)+}$ oxidation state is relatively stable, e.g., Cr^+,[32] Fe_{aq}^+,[33] and Co^+.[34,35] (An example for the latter case is the reaction $Co(CN_5)^{4-} + H_2O \rightarrow Co(CN)_5H^{3-} + OH^-$.)[34] The other strongly reducing monovalent cations decompose by the reactions

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$$2M_{aq}^{+} \rightarrow M_{aq}^{0} + M_{aq}^{2+} \tag{11}$$

(this reaction occurs most probably for Zn^+)[36]

$$2M_{aq}^{+} \rightarrow M_{2aq}^{2+} \tag{12}$$

(e.g., Cd^+,[37,38] Hg^+[39,40] followed by precipitation of Cd in the former case).

$$M_{aq}^{+} + OH \rightarrow M_{aq}^{2+} + OH^- \tag{13}$$

$$M_{aq}^{+} + H_2O_2 \rightarrow M_{aq}^{2+} + OH + OH^{-\,41,42} \tag{14}$$

In order to eliminate reaction 13 and decrease the role of reaction 14, generally methyl alcohol or *tert*-butyl alcohol was added to the solutions. These solutes scavenge the OH radicals via eq 15 and 16. The radical

$$OH + CH_3OH \rightarrow CH_2OH + H_2O \tag{15}$$

$$k_{15} = 8.3 \times 10^8\ M^{-1}\ s^{-1\,43}$$

$$OH + (CH_3)_3COH \rightarrow \cdot CH_2C(CH_3)_2OH \rightarrow H_2O \tag{16}$$

$$k_{16} = 5.2 \times 10^8\ M^{-1}\ s^{-1\,44}$$

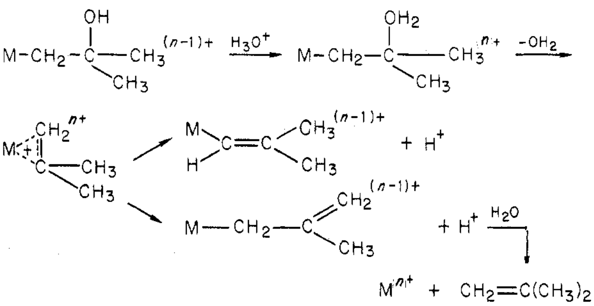
$\cdot CH_2C(CH_3)_2OH$ is a very weak reducing agent[45] and does not reduce any of the M_{aq}^{n+} cations studied. Methanol was used only in systems in which $\cdot CH_2OH$ radicals do not reduce the M_{aq}^{n+} cations. However it has been demonstrated recently that $\cdot CH_2OH$, $\cdot CH_2C(CH_3)_2OH$, and many other aliphatic radicals (including CO_2^-) are also rather strong oxidizing agents capable of oxidizing many low valent aquo cations and other low valent complexes, e.g., Ni_{aq}^{+},[46] Zn_{aq}^{+},[47] Cd_{aq}^{+},[38] Cd_{2aq}^{2+},[38] Cr_{aq}^{2+},[48,49] V_{aq}^{2+},[47] Ti^{III}_{aq},[50] Fe_{aq}^{2+},[50] and Co^{II} [35,51,52] complexes via the reactions

$$M_{aq}^{(n-1)+} + \cdot CR_1R_2R_3 \rightarrow M{-}CR_1R_2R_{3aq}^{(n-1)+} \tag{17}$$

followed by

$$M{-}CR_1R_2R_3^{(n-1)+} + H_2O/H_3O^+ \rightarrow M_{aq}^{n+} + HCR_1R_2R_3 + OH^-/H_2O \tag{18}$$

or by more complicated sequences, e.g.[48]



(19)

In principle the oxidation reactions by aliphatic radicals resemble the oxidation of Fe_{aq}^{2+},[53] Cr_{aq}^{2+},[32] Ti_{aq}^{3+},[54] V_{aq}^{2+},[47] Ni_{aq}^{+},[47] and Cd_{aq}^{+}[47] via eq 20. The

$$M_{aq}^{(n-1)+} + H \rightarrow M{-}H_{aq}^{(n-1)+} \xrightarrow{H_2O/H_3O^+} M_{aq}^{n+} + H_2 \tag{20}$$

specific rates of reaction 20 for $M_{aq}^{n-1} = Fe_{aq}^{2+}$ or Ti^{III}_{aq} are considerably higher than those of the water exchange in the inner coordination sphere of these cations, thus indicating that reaction 20 proceeds via seven-coordinated intermediates.[32] It is plausible that in some cases reaction 17 also proceeds via intermediates with expanded coordination spheres. The relatively high specific rates of reaction 17 indicate that it clearly interferes with the study of the decomposition of $M_{aq}^{(n-1)+}$ by reactions 11 and 12. It seems, therefore, that most of the information available at present on the specific rates of the latter reactions is inaccurate. A partial contribution of reaction 17 in addition to reaction 14 to the decomposition reaction of Yb_{aq}^{2+} might explain the discrepancy in the reported lifetime of Yb^{2+} as obtained in radiolytic[55] and electrochemical[56] studies.

Reduction Reactions. The low valent complexes of transition-metal cations in aqueous solutions are strong reducing agents. Their redox potentials are difficult to measure due to their short lifetime, although some have been estimated using thermodynamic data.[57] The redox potentials of Zn_{aq}^{+} and Cd_{aq}^{+} were also estimated from their specific rates of reaction with $Co(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{3+}$, assuming that these reactions are outer-sphere reductions and applying the Marcus theory.[58] Recently Rao and Hayon[59] reported "kinetic redox potentials" for a series of low valent transition-metal cations. The latter values seem to have little, if any, thermodynamic significance as they were measured under nonequilibrium conditions. It is of interest to note that Ag_{aq}^{0} reduces MnO_4^- to MnO_4^{2-} in a reaction which is diffusion controlled,[60] though the redox potentials for Ag^+/Ag^0_s and MnO_4^-/MnO_4^{2-} are

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0.80 and 0.57 V, respectively. Thus the kinetic results clearly indicate that Ag_{aq}^0 is a much stronger reducing agent than Ag_s^0, as could have been predicted. This result also explains why Ag^+ was found to be an inefficient oxidizing agent towards free radicals in homogeneous aqueous solutions.[61]

The kinetics of many redox reactions of low valent transition-metal complexes have been studied. However, only in few cases is enough information available to determine the detailed mechanism. The inorganic oxidants used can be divided into three main categories:

(a) The kinetics of reduction of transition-metal complexes, mainly $Co^{III}(NH_3)_5X$ and $Ru^{III}(NH_3)_3X$ by Zn^I,[62] Cd^I,[62] Ni^I,[62] Co^I,[35] Yb^{II},[63] and Sm^{II}[63] as their aquo and some other complexes were studied. The results indicate that most of these reactions proceed via the inner-sphere mechanism with the exception of $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and $Ru(NH_3)_6^{3+}$ and maybe Zn_{aq}^+.

(b) The kinetics of reduction of oxyanions, e.g., NO_3^-, NO_2^-, BrO_3^-, IO_3^-, MnO_4^-, by several low valent cations were studied.[41,42,55] The order of reactivity of the different anions was found to be more similar to their reactivity toward hydrogen atoms than toward e_{aq}^-.[41,55,64] These results were interpreted as suggesting that the anion penetrates the inner coordination sphere of the cation prior to the electron transfer.[64] The latter conclusion is supported in the case of Cd^I by the effect of aminocarboxylic ligands on its reactivity. It was suggested that the observation that Cd^IEDTA is less reactive than Cd_{aq}^+ is due to the fact that the former is an "outer-sphere" reducing agent.[64]

(c) Reduction reactions of neutral molecules like O_2, N_2O, and H_2O_2[41,42,55] follow similar patterns to those described above. In the reaction of Ni_{aq}^+,[42,65] Co_{aq}^+,[42] $Rh(NH_3)_4^{2+}$,[66] and some Co^I complexes[35] with O_2 relatively long-lived intermediates, MO_2^+, are observed, proving an "inner-sphere" mechanism. No such intermediates were observed in the reactions $Zn_{aq}^+/Cd_{aq}^+ + O_2 \rightarrow Zn_{aq}^{2+}/Cd_{aq}^{2+} + O_2^-$.[42,65] The latter results seem to suggest that the complex $M^{2+}O_2^-$ is unstable for the d^{10} Zn_{aq}^{2+} and Cd_{aq}^{2+} ions, but an outer-sphere mechanism for these reactions cannot be ruled out. It was suggested[42] that the reactions of $M^+ = Ni^+, Co^+, Zn^+, Cd^+$ with N_2O follow the mechanism

$$M^+ + N_2O \rightarrow MO^+ + N_2 \qquad (21)$$

forming stable Co^{III} and unstable Cd^{III}, Zn^{III}, and Ni^{III} compounds. This is the first and only evidence to date for the possible formation of Zn^{III} and Cd^{III} compounds in aqueous media. Furthermore, if the suggested mechanism is correct, it clearly indicates an atom-transfer process, i.e., an "inner-sphere" mechanism.

It might be concluded that most of the redox reactions of low valent transition-metal complexes studied seem to proceed via the "inner sphere" mechanism. The results available are as yet insufficient for a good correlation of reactivity with redox potentials or electronic structure of the complexes, though some correlations to redox potentials seem to be useful for comparison between very similar systems, e.g., Yb_{aq}^{2+} and Sm_{aq}^{2+}.[55,63] The relative reactivities might also involve the rate of ligand exchange of the low valent cation. This could be the explanation for the observation that $k_{Ag^0+MnO_4^-} > k_{Cd^++MnO_4^-}$ and $k_{Cu^++MnO_4^-} > k_{Ni^++MnO_4^-}$. Not even the order of reactivity of the low valent cations toward different oxidants is constant, though in general the order is $Zn_{aq}^+ \sim Co_{aq}^+ > Cd_{aq}^+ > Sm_{aq}^{2+} > Ni_{aq}^+ > Yb_{aq}^{2+}$.

Ligand Exchange Reactions. Due to the short lifetime of the low valent complexes in aqueous solutions little information is available concerning their ligand exchange reactions. The observation that redox reactions of Ni_{aq}^+, Cd_{aq}^+, Sm_{aq}^{2+}, Yb_{aq}^{2+} etc. proceed, at least in part, via the "inner-sphere" mechanism with specific rates approaching the diffusion-controlled limit indicates that the oxidant can form a bond with the central metal atom of the aquo complex rapidly. Similar conclusions can be drawn from the high specific rates of the reactions $2M^+ \rightarrow M_2^{2+}$ (for Cd_{aq}^+[37] and Hg_{aq}^+[39]) and $M^0 + M^+ \rightarrow M_2^+$ (for Ag[66a] and Tl[67]). However, as little is known about the coordination number of the low valent cations, it is not clear whether ligand exchange is required prior to the coordination of the oxidant to the central metal cation. Thus Ni_{aq}^+ has a d^9 configuration and is expected to be planar, as in $Ni(CN)_4^{3-}$, and the oxidation probably proceeds along the *Z* axis.

The specific rate of complexation reaction of M^+ with a double bond was measured for $M^+ = Ni_{aq}^+$[42] and Cu_{aq}^+.[68] The results, though measured for different ligands, indicate that the Cu_{aq}^+ reactions are diffusion controlled while the Ni_{aq}^+ reactions are one order of magnitude slower. These results are in agreement with the expected order of reactivity of d^{10} and d^9 monovalent cations.

For Ni(I) the specific rates of reactions 22 were

$$Ni(CN)_4^{3-} \underset{k_{-22}}{\overset{k_{22}}{\rightleftharpoons}} Ni(CN)_3^{2-} + CN^- \qquad (22)$$

measured, $k_{22} = 4\text{–}8 \times 10^3\ s^{-1}$, $k_{-22} = 8 \times 10^7\ M^{-1}\ s^{-1}$.[69,70] This seems to be the only case for which the kinetics of such an equilibrium reaction were reported. These results confirm the suggestion that $Ni(CN)_3^{2-}$ is formed as an intermediate in the electrochemical reduction of $Ni(CN)_4^{2-}$ to $Ni_2(CN)_6^{4-}$.[71] It was also suggested that the catalytic effect of $Ni(CN)_4^{2-}$ on the decomposition of sodium amalgam in alkaline solutions is explained by the sequence[72]

$$Na(Hg) + Ni(CN)_4^{2-} \rightarrow Na^+ + Ni(CN)_4^{3-} \qquad (23)$$

$$Na(Hg) + Ni(CN)_4^{3-} \rightarrow Na^+ + Ni(CN)_4^{4-} \qquad (24)$$

$$Ni(CN)_4^{4-} + H_2O \rightarrow Ni(CN)_4^{3-} + {}^1/_2H_2 + OH^- \qquad (25)$$

$$2Ni(CN)_4^{3-} \rightleftarrows Ni_2(CN)_6^{4-} + 2CN^- \qquad (26)$$

The fact that the yield of $Ni_2(CN)_6^{4-}$ per mol of sodium decreases steadily as the reduction proceeds was explained by assuming that equilibrium 26 is very rapidly

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established. The pulse-radiolytic results[70] do not support this idea, in agreement with the observations that $Ni_2(CN)_6^{4-}$ is not reduced polarographically[71] and that potassium metal reduces $Ni_2(CN)_6^{4-}$ rather slowly in liquid ammonia,[73] though $Ni(CN)_4^{3-}$ is readily reduced both polarographically and by potassium. The pulse radiolytic results indicate that $Ni_2(CN)_6^{4-}$ is not formed via reaction 26 but rather via reaction 22 followed by reaction 27. Thus it is suggested that the

$$2Ni(CN)_3^{2-} \rightarrow Ni_2(CN)_6^{4-} \qquad (27)$$

increase in the steady-state concentration of $Ni(CN)_4^{3-}$ during the decomposition of the sodium amalgam is due to the increase in the free cyanide concentration affecting equilibrium 22.

Cations in Intermediate Oxidation States

The stable oxidation states in aqueous solutions of several metals differ by two valence units or more (e.g., $Au^{I,III}$, $Tl^{I,III}$, $In^{I,III}$, $Pt^{II,IV}$, $Sn^{II,IV}$, $Pb^{II,IV}$, $As^{III,V}$, $Te^{IV,VI}$, $U^{IV,VI}$, $Mn^{II,VI}$, and $Cr^{III,VI}$. Kinetic data indicate that in most redox processes of these systems the metal cation in the unstable intermediate oxidation state is involved. However, only little information concerning the chemical properties of these ions can be obtained by conventional techniques. Pulse radiolysis seems to provide the easiest approach to the study of the chemical properties of these oxidation states. Ions in the intermediate oxidation states can be obtained either through reduction of the higher oxidation state by a reducing radical (e.g., e_{aq}^-, H, CO_2^-) or through oxidation of the lower oxidation state by an oxidizing radical (e.g., OH, Br_2^-, NH_2).

The most detailed study of a metal cation in an intermediate oxidation state seems to be that of Tl^{II},[33,67,74] which can be obtained by the reactions $OH + Tl_{aq}^+ \rightarrow Tl_{aq}^{2+}$, $k = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}$, and $H + Tl^{III}_{aq} \rightarrow Tl_{aq}^{2+}$, $k = 3.9 \times 10^7\ M^{-1}\ s^{-1}$.[74] The UV absorption spectrum and the specific rate of the disproportionation reaction $2Tl_{aq}^{2+} \rightarrow Tl_{aq} + Tl^{III}_{aq}$, $k = 1.9 \times 10^8\ M^{-1}\ s^{-1}$ were measured.[74] The kinetics of the oxidation of Fe_{aq}^{2+} by Tl^{III} were studied by conventional techniques. It was found that the mechanism of this reaction is

$$Tl^{III} + Fe_{aq}^{2+} \underset{k_{-28}}{\overset{k_{28}}{\rightleftharpoons}} Tl_{aq}^{2+} + Fe^{III}_{aq} \qquad (28)$$

$$Tl_{aq}^{2+} + Fe_{aq}^{2+} \xrightarrow{k_{29}} Tl_{aq}^{+} + Fe^{III}_{aq} \qquad (29)$$

However only k_{28} and k_{-28}/k_{29} could be determined. The measurement of k_{29} by the pulse-radiolytic technique enabled the calculation of k_{-28} and K_{28} and thus the standard redox potentials $E^0(Tl^{3+}/Tl^{2+}) = 0.30$ V and $E^0(Tl^{2+}/Tl^{+}) = 2.22$ V were derived.[74] Using these values it was shown that Tl_{aq}^{2+} cannot be an intermediate in the isotopic exchange reaction $^*Tl^+ + Tl^{3+} \rightleftharpoons Tl^+ + {}^*Tl^{3+}$.[74] These results are in full agreement with those obtained independently by the flash-photolytic technique.[75] The pK values for the formation of $TlOH^+$ and $Tl(OH)_2$ were found to be 4.6 and 7.7, respectively,[76] and the stability constants of the chloro complexes of Tl^{II}, $TlCl^+$, $TlCl_2$, and $TlCl_3^-$ are 6.2×10^4, 1900, and 13 M^{-1}, respectively.[77] The absorption spectra of these complexes were also reported. Furthermore the specific rate of the ligand exchange reaction $TlCl^+ \rightarrow Tl_{aq}^{2+} + Cl^-$ was found to be $1.4 \times 10^5\ s^{-1}$.[77]

Cations in High Oxidation States

Complexes in high unstable oxidation states are obtained by the reactions of several free radicals, e.g., OH, $\cdot NH_2$, Br_2^-, O_2^-, $\cdot CH_3$,[78-80] with a series of transition-metal complexes. Recently it has been suggested that some complexes with unusual high oxidation states can also be obtained in the reaction sequence $M^{n+} + e_{aq}^- \rightarrow M^{(n-1)+}$; $M^{(n-1)+} + Ox \rightarrow M^{(n+1)^+}\text{–}Ox^{2-}$ where Ox is a two-electron oxidizing agent. Thus it has been suggested that Ni^{III}, Zn^{III}, and Cd^{III} are formed with Ox $\equiv N_2O$.[42]

The mechanisms of oxidation of aquo complexes by OH radicals have been discussed in detail.[81] A mechanism involving a hydrogen atom abstraction from a water molecule in the inner coordination sphere as the rate-determining step was proposed.[81] This conclusion seems premature due to the following reasoning.

(a) It was argued that these reactions cannot proceed via the inner-sphere mechanism as some of them, e.g., with Ti^{III} and Fe^{II}, are faster than the exchange of the water molecules of the inner hydration sphere.[81] However, it was shown that some of these cations, including Ti^{III} and Fe^{II}, are oxidized by H atoms and some aliphatic radicals via a seven-coordinated intermediate.[32] It is plausible that this mechanism is applicable also to the oxidations by OH radicals. (b) The outer-sphere mechanism was ruled out due to the lack of the proper correlation between the specific rates of reaction and the redox potentials of the couples studied.[81] However it is plausible that the interaction between some aquo complexes and OH radicals is higher than that assumed in the Marcus theory, as is the case for the reactions of e_{aq}^-.[82] Therefore the specific rates of reaction are expected to be higher than those calculated by the Marcus theory, as observed for the reaction $OH + Cu_{aq}^{2+} \rightarrow Cu^{III}_{aq}$.[81,83] It should be pointed out that most of the reactions of OH radicals, even $OH + Fe(CN)_6^{4-}$, are faster than predicted by the Marcus theory. Though the free-energy gain in the latter reaction is large, ~40 kcal/mol, the reaction is expected to be slow due to the high hydration energy of OH^-, ~110 kcal/mol. Thus a "strong" interaction

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(83) The suggestion that Cu^{III}_{aq} is better described as a $Cu^{2+}\cdot OH$ or $Cu^{2+}\cdot O^-$ complex seems unjustified. First of all there is no difference between the two descriptions in an MO model. Secondly the trivalent copper ion was shown to undergo several acid–base equilibrium processes, and $pK_a = 4.3 \pm 0.2$ for $Cu(OH)_2^+ \rightleftharpoons Cu(OH)_3 + H_3O^+$ was reported.[84] This result seems to contradict the $Cu^{2+}\cdot OH$ model.

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between the OH radicals and most reducing agents seems to exist.[85]

The mechanisms of decomposition of a series of $\mathrm{Cu^{III}}$[78] and $\mathrm{Ni^{III}}$[79,80] complexes were studied. The complexes of both cations with NH_3 and ethylenediamine as ligands, as well as $\mathrm{Cu^{III}_{aq}}$, decompose via second-order processes. For $\mathrm{Cu^{III}_{aq}}$[78] the decomposition mechanism was shown to be pH dependent, in neutral solutions the results indicate that the decomposition proceeds via eq 30, whereas in acid solution the suggested mechanism is

$$2\mathrm{Cu^{III}_{aq}} \rightarrow 2\mathrm{Cu_{aq}}^{2+} + \mathrm{H_2O_2} \qquad (30)$$

$$\mathrm{Cu^{III}_{aq}} \rightleftarrows \mathrm{Cu_{aq}}^{2+} + \mathrm{OH};\ \mathrm{OH} + \mathrm{Cu^{III}_{aq}} \rightarrow \mathrm{Cu_{aq}}^{2+} + \mathrm{H_2O_2} \qquad (31)$$

Similar mechanisms are plausible also for the amino complexes, where the data are insufficient to differentiate between the two possibilities. It is plausible that some of these reactions, which are base catalyzed, proceed via eq 32–34.

Similar mechanisms have been proposed for the oxidative dehydrogenation of amino ligands of $\mathrm{Cu^{II}}$, $\mathrm{Ni^{II}}$, and other cations.[86] The mechanisms of decomposition of $\mathrm{Cu^{III}}$ and $\mathrm{Ni^{III}}$ complexes with aminocarboxylic ligands differ considerably. Thus all the $\mathrm{Cu^{III}}$ complexes of this type (including NTA,[80] EDTA,[80] and a series of amino acids[78] as ligands) decompose via a first-order process. It has been suggested[78] that the first reaction in this case is eq 35. This reaction is followed by a sequence of redox processes yielding $\mathrm{Cu^{I}}$, NH_3, and CO_2. The detailed mechanism of these processes has not been elucidated. On the other hand, $\mathrm{Ni^{III}EDTA}$[80,87] is stable for days, $\mathrm{Ni^{III}(NH_2CH_2CO_2^-)_{2,3}}$ decomposes via a second-order process,[79] and only $\mathrm{Ni^{III}NTA}$[80] decomposes via a first-order mechanism. It has been suggested that this difference between the mechanisms of decomposition of $\mathrm{Cu^{III}}$ and $\mathrm{Ni^{III}}$ complexes stems from the higher oxidation potential of the $\mathrm{Cu^{III}/Cu^{II}}$ couples, which enable the oxidation of the carboxylic group.[79] The observation that complexes of trivalent copper and nickel with relatively simple ligands can be obtained as rather long-lived intermediates in aqueous solutions induced studies looking for similar complexes using other techniques. Thus it was shown recently that the tetraglycine ligand stabilizes $\mathrm{Ni^{III}}$ and $\mathrm{Cu^{III}}$[88] in neutral aqueous solutions. It was also suggested that the enzyme galactose oxidase contains a trivalent copper ion in the active center.[89] Furthermore the participation of $\mathrm{Cu^{III}}$, $\mathrm{Ni^{III}}$, in catalytic oxidation reactions has been indicated in many studies. For example, it was suggested that the catalytic deamination of amines and amino acids by O_2 or H_2O_2 in alkaline solutions in the presence of $\mathrm{Cu^{2+}}$ and $\mathrm{Ni^{2+}}$ and of ascorbic acid in the presence of $\mathrm{Cu^{2+}}$ involves their complexes in the trivalent oxidation state.[90,91] The observation of these complexes by the pulse radiolytic technique, the estimation of their redox potentials, and the elucidation of the mechanisms of their decomposition support and elucidate the details of the suggested mechanisms of the thermal reactions. It was also suggested, based on pulse radiolytic results,[92,93] that the mechanism of the electrocatalytic oxidation of ethylenediamine in the presence of $\mathrm{Cu^{II}}$ or $\mathrm{Ni^{II}}$ involves $\mathrm{Cu^{III}}$ or $\mathrm{Ni^{III}}$ species.

$$\begin{aligned}&\mathrm{Men}_l(\mathrm{H_2O})_{6-2l}{}^{3+} + \mathrm{OH^-} \rightleftarrows \\ &\quad \mathrm{M(en)}_{l-1}(\mathrm{NHCH_2CH_2NH_2})(\mathrm{H_2O})_{6-2l}{}^{2+} + \mathrm{H_2O} \qquad (32)\end{aligned}$$

$$\begin{aligned}&\mathrm{M(en)}_l(\mathrm{H_2O})_{6-2l}{}^{3+} + \mathrm{M(en)}_{l-1}(\mathrm{NHCH_2CH_2NH_2})(\mathrm{H_2O})_{6-2l}{}^{2+} \rightarrow \\ &\quad \mathrm{Men}_l(\mathrm{H_2O})_{6-2l^+}{}^{2+} + \\ &\quad \mathrm{Men}_{l-1}(\mathrm{NH{=}CHCH_2NH_2})(\mathrm{H_2O})_{6-2l}{}^{2+} + \mathrm{H_3O^+} \qquad (33)\end{aligned}$$

$$\begin{aligned}&\mathrm{Men}_{l-1}(\mathrm{NH{=}CHCH_2NH_2})(\mathrm{H_2O})_{6-2l}{}^{2+} + 3\mathrm{H_2O} \rightarrow \\ &\quad \mathrm{Men}_{l-1}(\mathrm{H_2O})_{8-2l} + \mathrm{NH_3} + \mathrm{NH_2CH_2CHO} \qquad (34)\end{aligned}$$

$$\mathrm{Cu^{III}(NH_2RCO_2^-)}_n \rightarrow \mathrm{Cu^{II}(NH_2RCO_2^-)}_{n-1}(\mathrm{NH_2RCO_2\cdot}) \qquad (35)$$

Concluding Remarks

The involvement of metal complexes in unstable oxidation states as intermediates in many chemical processes is commonly accepted. Some pertinent processes are: (a) simple redox reactions, e.g., $\mathrm{Tl^{2+}}$ in the oxidation of $\mathrm{Fe_{aq}}^{2+}$ by $\mathrm{Tl^{III}}$;[74] (b) catalytic processes, e.g., $\mathrm{Cu^{III}}$ in the copper-catalyzed autoxidation of ascorbic acid,[91] or $\mathrm{Ni(CN)_4}^{3-}$ in the catalytic decomposition of sodium amalgam in the presence of $\mathrm{Ni(CN)_4}^{2-}$;[72] (c) electrochemical processes, e.g., $\mathrm{Ru(bpy)_3}^+$;[94] (d) electrocatalytic processes, e.g., $\mathrm{Cu^{III}}$ and $\mathrm{Ni^{III}}$ in the electrocatalytic oxidation of amines in the presence of $\mathrm{Cu^{II}}$ and $\mathrm{Ni^{II}}$ complexes;[92–93] (e) photochemical processes, e.g., $\mathrm{Ru(bpy)_3}^+$;[94] (f) enzymatic reactions, e.g., $\mathrm{Cu^{III}}$,[89] $\mathrm{Mn^{I}}$, and $\mathrm{Mn^{IV}}$.[95] The techniques used, however, do not enable the elucidation of the chemical properties of these intermediates in most systems, due to the short lifetime of the complexes in the unstable oxidation states and thus to their low steady-state concentrations in these systems. The purpose of this Account is to point out the capability of the pulse-radiolytic technique in elucidating the physical and chemical properties of these unstable intermediates.

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