On the Reactivity of Transition-metal Complex Ions toward Hydrated Electrons

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THE kinetics of the reactions of hydrated electrons with aquo- and other complexes of transition-metal ions have been the subject of a number of investigations using pulse radiolysis techniques.[1–4] It has been suggested[5] that the reactivity of a given ion toward e^-_{aq} is determined by the gain in energy on accommodation of an additional electron into a vacant orbital of the complex ion, without any involvement of the bonds between the central atom and the ligands. In the case of the aquo-complexes of the first series of transition-metal ions, Cr^{2+}_{aq} to Cu^{2+}_{aq} the specific rates of reaction with e^-_{aq} has been qualitatively correlated with the gain in exchange energy on accommodation of an additional electron into the d-orbitals, after correcting for the electrostatic repulsion involved.[5] For instance, the addition of an electron to d^4 Cr^{2+}_{aq} $[k(e^-_{aq} + Cr^{2+}_{aq}) = 4{\cdot}2 \times 10^{10}$ M^{-1} sec.$^{-1}$ is much more favoured energetically than the addition of an electron to d^5 Mn^{2+}_{aq} [$k(e^-_{aq} + Mn^{2+}_{aq}) = 7{\cdot}7 \times 10^7$ M^{-1} $sec.^{-1}$][1] which has all its T_{2g}- and e_g-orbitals occupied by single electrons. The next member of the series, d^6 Fe^{2+} reacts faster than Mn^{2+}_{aq} [$k(e^-_{aq} + Fe^{2+}_{aq}) = 3{\cdot}5 \times 10^8$ M^{-1} $sec.^{-1}$][1] partly because of the gain in exchange energy on addition of a fifth electron to the T_{2g}-orbitals and partly because of the decrease in the absolute energy level of these orbitals. In other words a linear free-energy relation was suggested between the electron affinity of a given ion and the rate of its reaction with hydrated electrons. The same arguments may be extended to explain the reactivities of the other members of this series as well as the behaviour of the second transition-metal series. The series of the rare earths, in which the additional electron enters an f-orbital, also show an analogous behaviour.

Following the assumptions cited above it is expected that a change in the energy levels of the d-orbitals of a given ion owing to a ligand field, which obviously changes its electron affinity, will result in a corresponding change in its reactivity toward e^-_{aq}. Such changes should be most pronounced when the ligand field is large enough to change the distribution of the d-electrons between the different sub-shells. To check on this assumption we have determined the specific rates of some cyano-complexes of the first transition series. The experimental procedure was identical with that previously described.[2,3] The specific rates of $Mn(CN)_6^{4-}$ and of $Fe(CN)_6^{4-}$ were determined and found to be $2{\cdot}5 \pm 0{\cdot}2 \times 10^{10}$ M^{-1} $sec.^{-1}$ and $<10^5$ M^{-1} $sec.^{-1}$ respectively. In the first case an electron is added to the last vacancy in a low-level T_{2g}-orbital, whereas in the second case the additional electron would have to be accommodated in a high-level completely vacant e_g-orbital. It should thus be noted that the substitution of a weak-field by a strong-field ligand reversed the order of reactivities of Fe^{II} and Mn^{II}. An analysis of the behaviour of other cyano-complexes[3] corroborates our assumption on the role of the energy level of the vacant d-orbitals in the reactions of transition-metal ions with hydrated electrons.

It may be concluded that the reaction of e^-_{aq} with inorganic complexes is primarily a "non-adiabatic" process[6] which does not involve the metal–ligand bonds. The electron thus seems to undergo rapid tunneling from its position in the solvent into a vacant position in the d-orbital of the substrate ion, before any other rearrangements take place. The probability of this process will depend on the electron affinity of the complex ion. A quantitative evaluation of electron affinities of complex ions of the transition metals is in progress. These values will be then correlated with the reactivities of these species with e^-_{aq}.

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