Reactions and Relative Potentials of Some Metal Ions in Unstable Valency States

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THE transient univalent states of certain metals, *e.g.*, Zn^+, Ni^+, Pb^+, Cd^+, Co^+, can be produced in aqueous solution by reduction of the corresponding M^{2+} ions with hydrated electrons.[1-3] These species absorb in the u.v. and their re-oxidation can be followed using pulse radiolysis.[4,5] We have examined their reactions with some oxidants including the M^{2+} ions, *e.g.*,

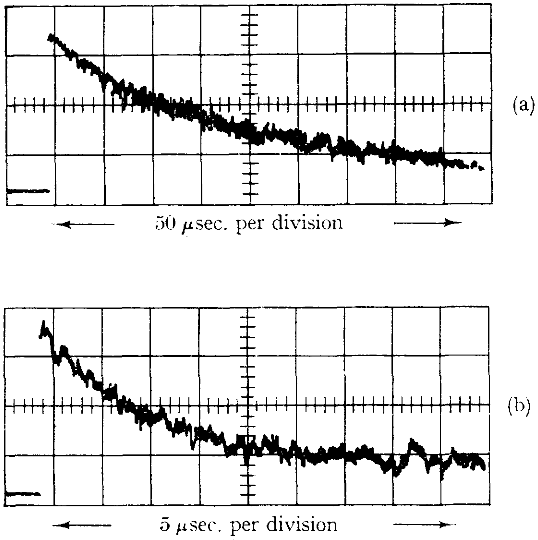
$$Cd^+ + Pb^{2+} \rightarrow Cd^{2+} + Pb^+$$

The latter reactions enable the relative potentials of the couples M^+/M^{2+} to be established in certain cases.

The M^+ ions were produced at 1—5 μM from neutral M^{2+} solutions (2—20 mM) using a 0·2 μsec. pulse of 4 Mev electrons. In the absence of other solutes, M^+ will decay by oxidation with the radical OH produced simultaneously with e^-_{aq}, by oxidation with water, or by dismutation, and in general the lifetime depends on the electron pulse intensity. Conditions were chosen to give initial half-lives of at least 50 μsec. Oxidants, *e.g.*, Pb^{2+}, were added at low concentration (50—200 μM) so that the amount of Pb^{2+} reacting with e^-_{aq} is small and hence the initial concentration of M^+ is unaffected.

However, the decay of absorption due to M^+ is increased due to reaction with Pb^{2+} (see Figure). Provided these increases are appreciable the rate constants for the re-oxidation of M^+ ions can be obtained.

The results of such experiments are given in the Table. In addition to these data we have also investigated the species produced from Co^{2+}—presumed to be Co^+—but could not observe reaction with any of the oxidants. Experiments



FIGURE

Cd^+ absorption at 3000 Å *produced by* 0·2 *μsec. electron pulse on neutral* 1·0 *m*M-$CdSO_4$. *Initial* [Cd^+] ca. 5 μM. *Ordinates* 1% *absorption per division.*

(a) *Second-order decay without additives.*

(b) *First-order decay in the presence of* 110 μM-Pb^{2+}.

were also done using Cr^{3+} as an oxidant but no reaction with the M^+ ions could be detected. These observations do not exclude reaction in these systems but indicate that the rate constants must be $< 10^7$ mole^{-1} sec.$^{-1}$

TABLE

Rate constants for M^+ *reactions*
Values of $k \times 10^{-8}$ mole^{-1} sec.$^{-1}$ at 18° c.

Oxidant	Zn^+	Cd^+	Pb^+	Ni
Zn^{2+}	57*	0†	0	0
Cd^{2+}	8·3	180*	0	0
Pb^{2+}	4·0	7·5	7·7*	0
Ni^{2+}	0·5	0	0	63*
O_2	33	33	39	22

* These are bimolecular constants for the decay of M^+ with no additive. That for Zn^+ corrects an earlier value (ref. 4).

† "0" means that no reaction was observed at the maximum concentration of oxidant which was feasible.

It will be noted that the oxygen reactions of the type

$$Cd^+ + O_2 \rightarrow Cd^{2+} + O_2^-$$

have approximately the same rate constant, which numerically is about that required for a diffusion-controlled rate. In comparison the reactions of the type

$$Cd^+ + Pb^{2+} \rightarrow Cd^{2+} + Pb^+$$

are lower by about fourfold, which is again to be expected for diffusion controlled reactions between such charged species.

Concerning the couples M^+/M^{2+}, it is clear that since Zn^+ reduces Cd^{2+}, and Cd^+ reduces Pb^{2+}, then

$$E^0(Pb^+/Pb^{2+}) > E^0(Cd^+/Cd^{2+}) > E^0(Zn^+/Zn^{2+})$$

We cannot place Ni^+/Ni^{2+} in this series since the only Ni reaction we could observe was the reduction of Ni^{2+} by Zn^+, from which we conclude that $E^0(Ni^+/Ni^{2+}) > E^0(Zn^+/Zn^{2+})$.

These conclusions are not inconsistent with a recent estimation of the potentials of these systems.[3]

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[1] J. H. Baxendale and R. S. Dixon, *Proc. Chem. Soc.*, **1963**, 148.
[2] G. E. Adams, J. H. Baxendale, and J. W. Boag, *Proc. Chem. Soc.*, **1963**, 241.
[3] J. H. Baxendale and R. S. Dixon, *Z. phys. Chem. (Frankfurt)*, **1964**, **43**, 161.
[4] J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc.*, 1965, *A*, **286**, 320.
[5] J. H. Baxendale, J. P. Keene, and D. A. Stott, "Pulse Radiolysis", Academic Press, London, 1965, p. 107.