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Reduction by Monovalent Zinc, Cadmium, and Nickel Cations

This information should prove interesting to chemists and personnel engaged in water pollution research.

The aim of the present study was to obtain a better understanding of the chemical properties of the monovalent transition metal cations in aqueous solutions by a systematic study of the kinetics of reduction of different inorganic substrates by Zn^+ , Cd^+ and Ni^+ .

The specific rates of reaction of Zn^+ , Cd^+ and Ni^+ with O_2 , N_2O , H_2O_2 , NO_2^- , NO_3^- , BrO_3^- , IO_3^- , Cu^{2+} , and H_3O^+ have been studied and determined. It was found that the order of reactivity is $Zn^+ \geq Cd^+ \geq Ni^+$, which can be correlated with the electronic structure of the monovalent cations.

All solutions were prepared from triply-distilled water and A. R. reagents without further treatment. Solutions of $2 \times 10^{-3} M$ of MSO_4 ($M = Zn^{2+}$, Cd^{2+} or Ni^{2+}) and $1 \times 10^{-3} M$ methanol were used in all experiments.

Pulse radiolytic experiments were conducted on a 0.4 sec., 25 MeV electron pulse from a linear accelerator yielding a dose of $0.8 - 6 \times 10^{19} \text{ eV.l.}^{-1}$ per pulse. The OH radicals formed by the pulse reacted with methanol, whereas the hydrated electrons reacted with M^{2+} to give M^+ . The decay of M^+ was followed spectrophotometrically at 3130 Å using a multiple-reflection cell with a 4 cm long optical cell giving a 16 cm total light path.

All traces were analyzed for first and second order decay, and pseudo first order rates were calculated when a good first order decay plot was obtained for at least three half-lives.

The measured rates of reaction of Zn^+ indicate that it is a powerful reducing agent. The Zn^+ reactions studied fall into the following groups: those which are

nearly diffusion-controlled; those too slow to be measured with the experimental technique; and N_2O (and possibly Cu^{2+}) which falls somewhere between the extremes.

The reaction rates of Cd^+ are slower, but similar to, the corresponding reaction rates of Zn^+ . Significant differences occur only with nitrate and bromate ions.

The reactions of Ni^+ are much slower than the others. Only the reaction rate of Ni^+ with O_2 approaches the diffusion-controlled limit, while most of the Ni^+ reactions were too slow to be measured.

Since the absorption bands of Zn^+ , Cd^+ and Ni^+ are similar and have been attributed to charge transfer to solvent transitions, one might believe they would also react similarly in reductions involving a charge transfer mechanism. It is found, however, that there is a definite order of reactivity: $Zn^+ > Cd^+ > Ni^+$. This does not automatically infer the same order for the redox potentials of the corresponding M^{2+}/M^+ couples.

The order of reactivity can be explained by assuming that in Zn^+ , the additional electron is located in an S orbital where it would be relatively exposed, resulting in the fact that Zn^+ is a strong reductant. Also in Cd^+ , the added electron is assumed to be in an S orbital, but has a lower reactivity. In Ni^+ , the added electron may enter the 3d shell, an inner orbital. Thus it is reasonable that Ni^+ is less reactive than Zn^+ and Cd^+ .

Notes:

1. Further information is available by D. Meyerstein and W. A. Mulac in "Reductions by Monovalent Zinc, Cadmium and Nickel Cations," *Jour. of Phys. Chem.*, 72, 784 (1968).

(continued overleaf)

2. Inquiries concerning this information may be directed to:

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Patent status:

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