

Kinetic studies of the transition metal ion catalyzed oxidation of some cyclic alcohols by ammonium meta vanadate in acidic medium

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Abstract

The first order kinetics of oxidation of the industrially important cyclic alcohols, cyclopentanol, cyclohexanol and cyclooctanol has been studied using Ammonium meta vanadate in H_2SO_4 medium. Cyclopentanol is used in the manufacture of perfumes and pharmaceuticals and cyclohexanol finds use in the polymer industry as a precursor in the manufacture of nylon.

The rate of oxidation of the alcohols was determined by the iodometric titration of the unreacted oxidant at regular time intervals during the course of the reaction. The reaction was studied at different temperatures and the thermodynamic activation parameters were evaluated and interpreted in terms of the reaction dynamics. The effect of ionic strength on the oxidation rate of alcohols was studied in dilute solution. The sequence of catalytic effect of the transition metal ions, $Mn(II)$, $Co(II)$ and $Ni(II)$ on the oxidation rate of cyclic alcohols was determined in acidic medium. A suitable reaction mechanism has been suggested for the oxidation process. The sequence of oxidation rates of the cyclic alcohols, Cyclooctanol > Cyclopentanol > Cyclohexanol has been explained on the basis of their ring size and stability.

Keywords: Cyclic alcohols, oxidation, ammonium meta vanadate, kinetics, transition metal ion catalysts, thermodynamic activation parameters.

Introduction

Literature survey shows several reports of the oxidation of alcohols to aldehydes / ketones^{5,6,8,12,13}, but there are few reports of the kinetic studies of oxidation of alcohols. This study deals with the first order kinetics of the oxidation of the cyclic alcohols, cyclopentanol, cyclohexanol and cyclooctanol by ammonium meta vanadate in acidic medium. The effects of alcohol and oxidant concentrations, ionic strength and temperature (303-318K) on the rates of cyclic alcohols have been investigated.

From the change of oxidation rate with temperature, thermodynamic activation parameters have been determined. The experimentally determined sequence of oxidation rates of alcohols have been explained on the basis of their ring size and stability. $Mn(II)$, $Co(II)$ and $Ni(II)$ ions

have been used to catalyze the oxidation of cyclic alcohols and their sequence of catalytic efficiency was determined for each alcohol under study.

A suitable reaction mechanism has been suggested for the oxidation of alcohols by Ammonium meta vanadate in acidic medium.

Materials and Methods

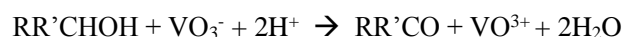
The cyclic alcohols were procured from E. Merck Suhuchalt, Germany and used as received. All other chemicals and reagents used were of A. R. Analytical Grade. The oxidation was studied under first order conditions with respect to the inorganic oxidant and the rate constant (k) was determined from the linear plots of \log (unreacted oxidant) versus time. The reaction was studied in the temperature range 303-313K. From the Arrhenius plots of $\log k$ versus T^{-1} , the energy of activation and other thermodynamic parameters were determined.

A similar procedure was followed to study the catalytic effect of transition metal ions on the oxidation rates of cyclic alcohols in the range $[M(II)] = 2.5$ to $4.5 \times 10^{-3} \text{ mol dm}^{-3}$ at 303K. The effect of ionic strength (μ) on the oxidation rates of alcohols was studied in dilute solution in the range $\mu=5$ to $25 \times 10^{-2} \text{ mol dm}^{-3}$ at 313 K using K_2SO_4 .

Results and Discussion

Kinetics of oxidation of Cyclic alcohols: The cyclic alcohols were oxidized to the corresponding ketones by ammonium meta vanadate in acidic medium. For all the alcohols the oxidation rate increased with [alc.] but decreased with increasing oxidant concentration (Table 1, Figure 1).

In acidic medium, ammonium meta vanadate NH_4VO_3 forms vanadic acid HVO_3 which is a strong acid and strong oxidant. For secondary alcohols, the oxidation reaction can be shown as:



The oxidation product i.e. ketone was identified by 2, 4-dinitrophenyl hydrozone test and was confirmed by TLC.

The oxidation rates followed the sequence:

Cyclooctanol > Cyclopentanol > Cyclohexanol (Table 1, Figure 1).

Table 1
The rate constant data for the oxidation of cyclic alcohols by Ammonium meta vanadate in acidic medium
 $[\text{H}_2\text{SO}_4] = 0.1 \text{ mol dm}^{-3}$
Temperature = 303K

[alc.] $\times 10^1$ mol dm^{-3}	$[\text{NH}_4\text{VO}_3] \times 10^3$ mol dm^{-3}	Cyclopentanol $k \times 10^4 \text{s}^{-1}$	Cyclohexanol $k \times 10^4 \text{s}^{-1}$	Cyclooctanol $k \times 10^4 \text{s}^{-1}$
0.25	5.00	2.58	1.02	4.03
0.50	5.00	3.33	4.30	4.19
0.63	5.00	5.38	4.01	6.18
0.75	5.00	5.55	5.11	7.92
0.88	5.00	8.25	5.98	8.02
1.00	5.00	8.45	6.28	9.55
1.00	2.50	9.09	7.71	4.92
1.00	5.00	8.29	6.58	4.74
1.00	10.00	3.68	3.98	3.68
1.00	15.00	2.94	3.63	3.12
1.00	20.00	1.45	2.34	2.18
1.00	25.00	1.28	2.07	1.08

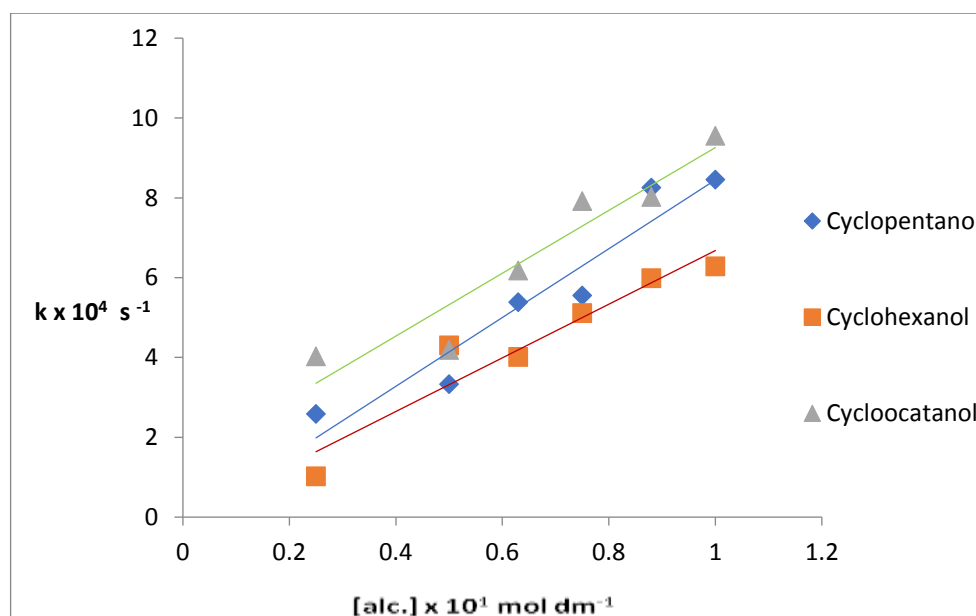
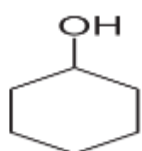
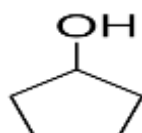


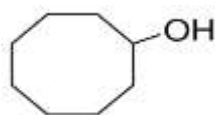
Fig. 1: Variation of rate constant of oxidation of cyclic alcohols with [alc.]



Cyclohexanol



Cyclopentanol



Cyclooctanol

Structures of Cyclic alcohols:

It has been observed and reported that 5, 7 and 8 membered rings are more reactive than 6 membered rings^{3,4,10,14}. This trend is seen in the sequence of the oxidation rates of the cyclic alcohols studied.

Effect of ionic strength on oxidation rates of cyclic alcohols: K_2SO_4 was used to study the effect of ionic

strength on the oxidation rates of cyclic alcohols in dilute solution in the range $\mu = 5$ to $25 \times 10^{-2} \text{ mol dm}^{-2}$ at 303K. (Table 2). The graphs of $\log k$ versus $\sqrt{\mu}$ were found to be straight lines parallel to the $\sqrt{\mu}$ axis indicating that the oxidation rate was independent of ionic strength (Figure 2).

Variation of oxidation rates of cyclic alcohols with temperature: The thermodynamic activation parameters were determined from the variation of oxidation rates of alcohols with temperature in the range 303-318K (Table 3).

The negative values of ΔS^\ddagger indicate a decrease in the degrees of freedom of the reacting system due to the formation of a transient rigid activated complex during the oxidation reaction and subsequent reorientation of solvent molecules around the activated complex^{1,7}.

Table 2

Effect of ionic strength on the rates of oxidation of Cyclic alcohols by Ammonium meta vanadate in acidic medium
 $[\text{alc.}] = 0.1 \text{ mol dm}^{-3}$ $[\text{H}_2\text{SO}_4] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{NH}_4\text{VO}_3] = 2.4 \times 10^{-3} \text{ mol dm}^{-3}$
 Temperature = 313K

$\mu \text{ mol dm}^{-3}$	$\sqrt{\mu}$	Cyclopentanol $k \times 10^4 \text{ s}^{-1}$	Cyclohexanol $k \times 10^4 \text{ s}^{-1}$	Cyclooctanol $k \times 10^4 \text{ s}^{-1}$
0.00	0.00	7.50	5.25	9.02
0.05	0.22	7.70	5.30	9.12
0.10	0.32	7.52	5.30	9.26
0.15	0.39	7.64	5.07	9.02
0.20	0.45	7.45	5.30	9.24
0.25	0.50	7.80	5.75	9.24

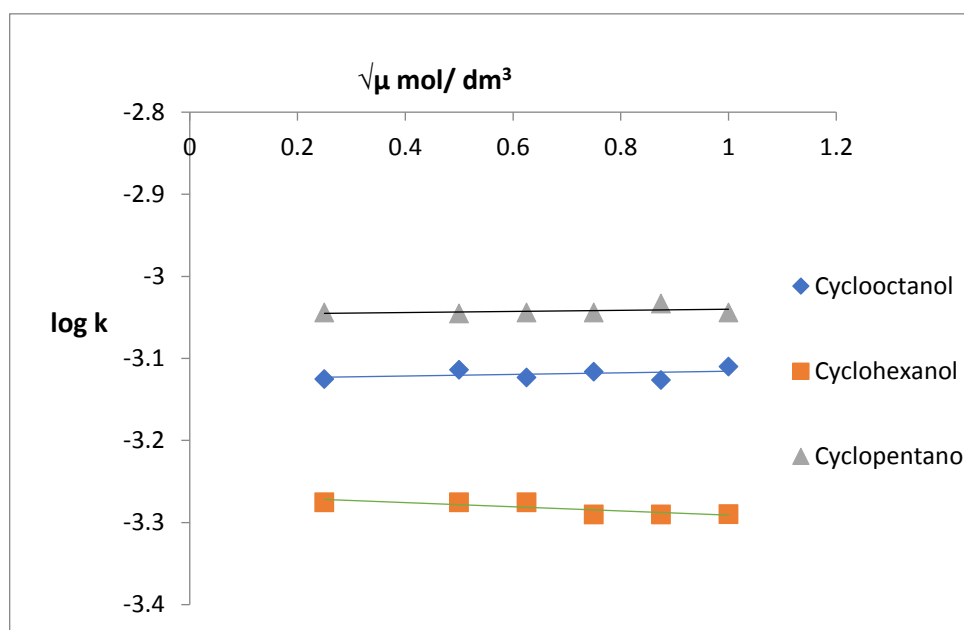


Fig. 2: Variation of oxidation rates of Cyclic alcohols with ionic strength

Table 3

Thermodynamic activation parameters for the oxidation of Cyclic alcohols by Ammonium meta vanadate in acidic medium

$[\text{alc.}] = 0.1 \text{ mol dm}^{-3}$ $[\text{H}_2\text{SO}_4] = 0.1 \text{ mol dm}^{-3}$

Temp. K	$k \times 10^4 \text{ s}^{-1}$	$E \text{ kJ mol}^{-1}$	$K^* \times 10^{17}$	ΔH^* kJ mol^{-1}	ΔG^* kJ mol^{-1}	ΔS^* $\text{kJ K}^{-1} \text{ mol}^{-1}$
Cyclopentanol						
303	1.05	22.21	1.84	20.05	96.12	-0.2535
308	1.29	22.21	1.82	20.01	97.76	-0.2549
313	2.49	22.21	2.80	19.97	98.24	-0.2525
318	2.51	22.21	2.97	19.93	99.67	-0.2531
Cyclohexanol						
303	1.15	22.55	1.83	20.35	96.02	-0.2525
308	1.15	22.55	1.83	20.25	97.45	-0.2520
313	1.82	22.55	2.80	20.15	98.34	-0.2515
318	1.96	22.55	2.97	20.05	98.67	-0.2504
Cyclooctanol						
303	1.05	22.07	1.66	19.57	96.37	-0.2560
308	1.82	22.07	1.66	19.55	97.34	-0.2567
313	2.16	22.07	3.25	19.49	97.77	-0.2525
318	4.31	22.07	6.55	19.45	97.60	-0.2481

The decrease in the entropy of activation can be explained by a model in which the water molecules are tightly held to the –OH bond which is the site of oxidation⁸.

Kinetics of transition metal ion catalyzed oxidation of cyclic alcohols: The transition metal ions Mn(II), Co(II) and Ni(II) were used to catalyze the oxidation of cyclic alcohols in the range [Mn(II)] = 2.5 to 4.5 x 10⁻³ mol dm⁻³. For all the metal ions under study, the oxidation rates of alcohols increased with [M(II)] (Table 3, Figures 3a, 3b and 3c).

The catalytic efficiency of metal ions is inversely proportional to the stability of their complexes which may be formed as short lived intermediates during the reaction. The stability of the complexes generally depends on the charge density of the metal ions besides several other factors. Thus the stability order for the complexes of the metal ions under study is expected to be Ni(II) > Co(II) > Mn(II)^{9,11} and hence the catalytic efficiency is expected to follow the sequence Mn(II) > Co(II) > Ni(II). But it is only approximate guide to metal ion behavior¹⁵ and discrepancies have been observed and reported.

In the present study, the sequences of catalytic efficiencies of metal ions are as follows:

Cyclopentanol Ni(II) > Mn(II) > Co(II) (Table 4, Figure 3a)
Cyclohexanol Mn(II) > Co(II) > Ni(II) (Table 4, Figure 3b)
Cyclooctanol Mn(II) > Co(II) > Ni(II) (Table 4, Figure 3c)

Conclusion

The oxidation rates of the cyclic alcohols using ammonium meta vanadate in acidic medium follow the sequence Cyclooctanol > Cyclopentanol > Cyclohexanol. Ionic strength has no effect on the oxidation of cyclic alcohols in dilute solution. The oxidation of cyclic alcohols is catalyzed by transition metal ions in acidic medium.

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Table 4
Catalytic effect of transition metal ions on the oxidation of Cyclic alcohols in acidic medium
[alc.] = 0.1 mol dm⁻³ [H₂SO₄] = 0.1 mol dm⁻³ Temperature = 303K

[M(II)] x 10 ³ mol dm ⁻³	k x 10 ⁴ s ⁻¹ Mn(II)	k x 10 ⁴ s ⁻¹ Co(II)	k x 10 ⁴ s ⁻¹ Ni(II)
Cyclopentanol			
0.00	1.02	1.02	1.02
2.50	4.04	2.2	4.97
3.50	5.22	3.33	6.14
4.50	6.26	4.97	7.57
Cyclohexanol			
0.00	3.02	3.02	3.02
2.50	7.13	5.27	4.41
3.50	10.91	8.42	5.28
5.50	11.15	9.41	7.62
Cyclooctanol			
0.00	3.78	3.78	3.78
2.50	5.78	5.59	4.41
3.50	8.05	6.05	4.98
4.50	10.14	7.48	5.57

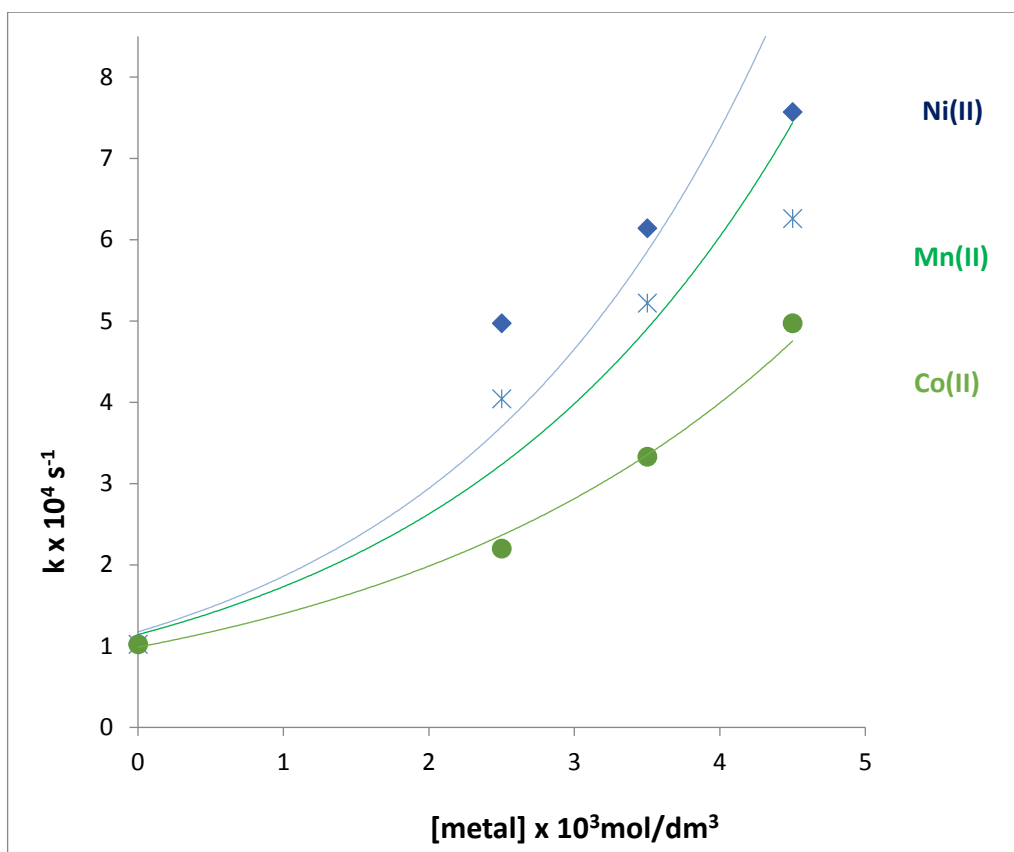


Fig. 3a: Variation of rate constant of oxidation of Cyclopentanol with [M(II)] Sequence of Oxidation rates : Ni(II) > Mn(II) >Co(II)

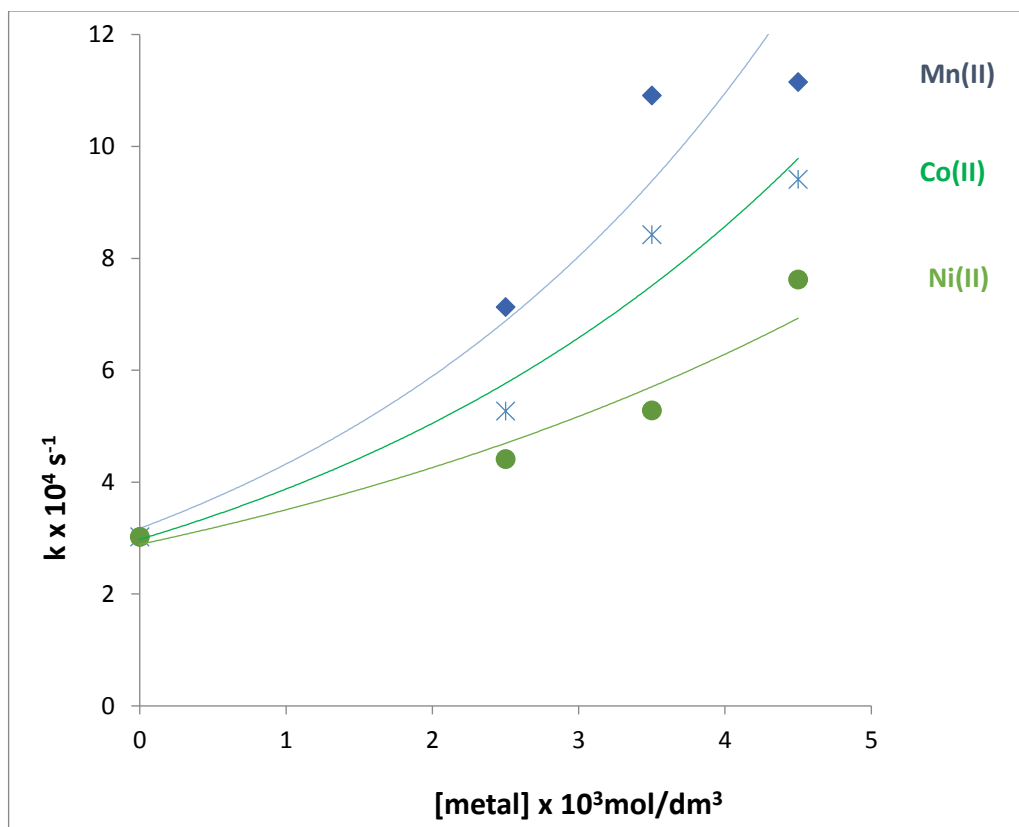


Fig. 3b: Variation of rate constant of oxidation of Cyclohexanol with [M(II)] Sequence of oxidation rates: Mn(II) > Co(II) >Ni(II)

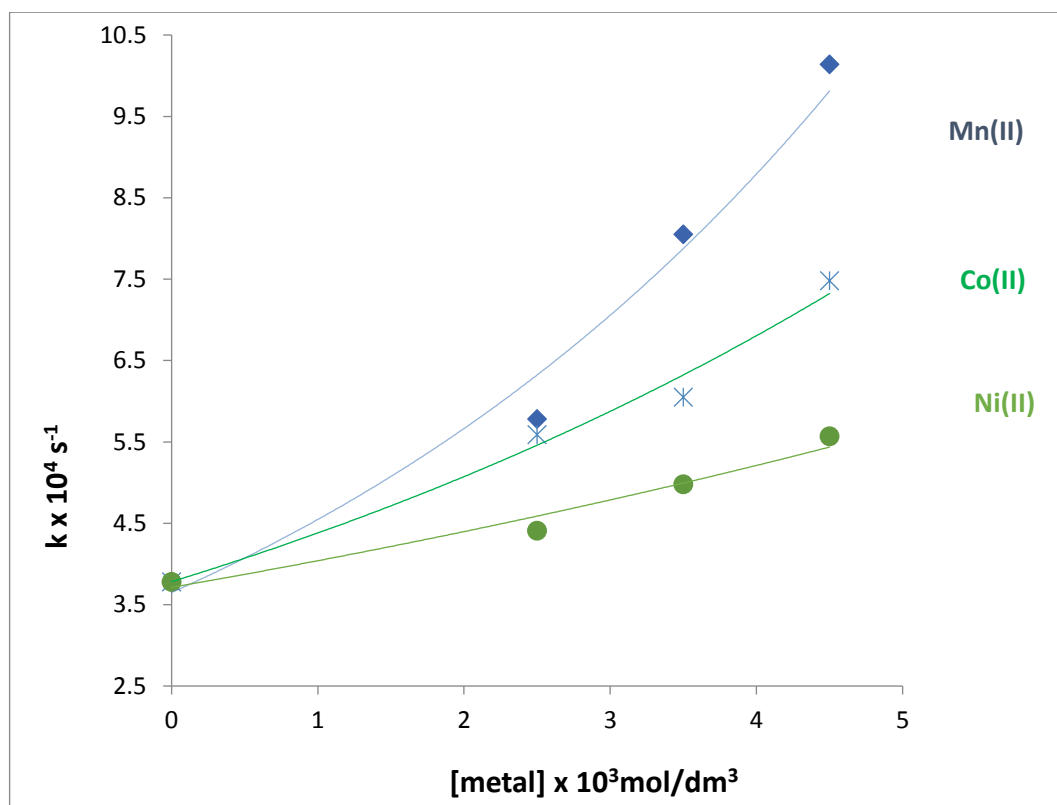


Fig. 3c: Variation of rate constant of oxidation of Cyclooctanol with [M(II)] Sequence of oxidation rates: Mn(II) > Co(II) > Ni(II)

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