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Os(VIII) catalysed oxidation of chloramines –T reactions

(A review study)

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Abstract

Rection of Os and chloramines –T (CAT) has been studied by many researchers. Os(VIII) readily reacts with CAT.Being pale yellow in color ,it is also used in spectro photo chemical reactions studies,Os exhibites variety of oxidation states which makes it more facile for its use as catalyst. In this review artical some reaction of Os(VIII) catalysed oxidation of chloramines –T has been compiled for use of researchers.

Introduction

Osmium (Os), atomic number 76 forms compounds with oxidation states ranging from −2 to +8. The most common oxidation states are +2, +3, +4, and +8. The most common compound exhibiting the +8 oxidation state is osmium tetroxide(OsO_4). Metallic osmium is harmless but finely divided metallic osmium is pyrophoric and reacts with oxygen at room temperature, forming volatile osmium tetroxide. Some osmium compounds are also converted to the tetroxide if oxygen is present. This makes osmium tetroxide the main source of contact with the environment.

This toxic compound is formed when powdered osmium is exposed to air. It is a very volatile, water-soluble, pale yellow, crystalline solid with a strong smell. Osmium powder has the characteristic smell of osmium tetroxide.[19] Osmium tetroxide forms red osmates $OsO_4(OH)_2^{2-}$ upon reaction with a base.

Osmium tetroxide is highly volatile and penetrates skin readily, and is very toxic by inhalation, ingestion, and skin contact. Airborne low concentrations of osmium tetroxide vapor can cause lung congestion and skin or eye damage, and should therefore be used in a fume hood.

Reactions using Os(VIII) as catalyst

1. Osmium (VIII) Catalyzed Oxidation of Acetone and Ethylmethyl Ketone by Chloramine-T

SP Mushran, R Sanehi, MC Agraval - Zeitschrift für Naturforschung B, 1972

The Osmium (VIII) catalyzed oxidation of acetone and ethylmethyl ketone by chloramine-T, in highly alkaline solutions showed first order dependence to chloramine-T and osmium (VIII). The order of the reactions with respect to alkali and ketone were found to be fractional …

2. Osmium-catalyzed vicinal oxyamination of olefins by Chloramine-T

KB Sharpless, AO Chong, K Oshima - The Journal of Organic …, 1976 - ACS Publications

This proposed mechanism for formation of 7 is directly analogous to the accepted mechanism
for the oxidation of olefins by selenium dioxide inestigeted by KB Sharpless and RF Lauer,

3. Kinetics of Os(VIII)-catalysed Oxidation of Benzaldehyde & Substituted Benzaldehydes by Chloramine-T

$$Os0_4 + OH^-]+ H_2O \sim[Os0_4 (OH)H_2O]1$$

$$[Os0_4 (OH) H_2O JI-+(OH-J\sim[Os0_4 (OH)2J2-+ H_2O$$

4. Kinetics and mechanism of oxidation of primary alcohols by chloramine-T catalyzed by OsO_4

Journal of Catalysis Volume 61, Issue 1, January 1980, Pages 165-169

OsO_4, which slowly decomposes into aldehyde and Os(IV). The Os(IV) thus produced is oxidized rapidly to Os(VIII) with the anion of chloramine-T.

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5 Os(VIII)-catalyzed and uncatalyzed oxidation of biotin by chloramine-T in alkaline medium

Journal of Molecular Catalysis Volume 265, Issues 1–2, 16 March 2007, Pages 70-

6. Mechanistic aspects for the oxidation of sunset yellow dye by chloramine-T in presence of perchloric acid and in sodium hydroxide medium catalyzed by Os(VIII)

Inorganica Chimica Acta

Volume 362, Issue 6, 20 April 2009, Pages 2044-2051

Under identical set of experimental conditions in alkaline medium, Os(VIII) catalyzed reaction is about seven-fold faster than the uncatalyzed reaction.

7. Kinetics and reactivities of ruthenium(III)- and osmium(VIII)-catalyzed oxidation of ornidazole with chloramine-T in acid and alkaline media:

Journal of Molecular Catalysis A: Chemical

Volume 310, Issues 1–2, 1 September 2009, Pages 24-33

The relative rates revealed that the catalyzed reactions are about 5-fold faster in Ru(III) whereas in Os(VIII) catalyzed reactions, it is around 9 times.

8. Os(VIII) as an Efficient Homogeneous Catalyst for the Oxidative Decolorization of Methylene Blue Dye with Alkaline Chloramine-T: Kinetic, Mechanistic, and Platinum Metal Ions Reactivity Studies

ind. Eng. Chem. Res. 2010, 49, 7, 3137

oxidative decolorization kinetic study of methylene blue(MB) by sodium-*N*-chloro-*p*-toluenesulfonamide (chloramine-T or CAT) in alkaline medium catalyzed by Os(VIII) spectrophotometrically at 664 nm (λ_{max} of the dye). The kinetics of oxidation of MB by CAT was also studied with other platinum metal ions. The relative reactivity of these catalysts are in the order Os(VIII) > Ru(III) > Ir(III) ≥ Rh(III) ≥ Pt(IV) > Pd(II). This trend may be attributed to the different d-electronic configurations of the metal ions. It was found that the catalyzed reactions are about 3-fold to 10-fold faster than the uncatalyzed reactions.

9. Kinetics of oxidation of cinnamaldehyde by chloramine-T in perchloric acid and in alkaline medium catalysed by Os(VIII)

Mythily, C K, Rangappa, K S , Mahadevappa, D S, Jul-1990, NISCAIR-CSIR, India

10. Kinetics and mechanism of Os(VIII)-catalysed oxidation of some substituted trans-cinnamic acids by chloramine-T in alkaline medium

Tetrahedron, Volume 50, Issue 37, 1994, Pages 10945-10954

The kinetics and mechanism of Os(VIII) catalysed oxidation of some substituted trans-cinnamic acids by chloramine-T in presence of alkaline medium has been investigated. The order with respect to [CAT] is zero and $[OsO_4]$ is one.

11. Kinetics of Os (VIII)-catalysed Oxidation of Alcohols by Chloramine-T

PS Radhakrishnamurti, B Sahu - 1978 - nopr.niscair.res.in

The order with respect to [CAT] is one and $[OsO_4]$ is one.

12. Kinetics of Os(VIII)-catalysed Oxidation of Benzaldehyde & Substituted Benzaldehydes by Chloramine-T

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Received 25 November 1976; accepted 7 February 1977

The kinetics of OsO_4.-catalysed oxidation of benzaldehyde and substituted benzaldehydes by chloramtne-T in aqueous and aqueous t-butanol under alkaline conditions has been investigated, The order with respect to CAT and OsO_4 is one each

13. Kinetics & Mechanism of OsO4-catalysed Oxidation of Benzyl Alcohol by Chloramine-T

KV Uma, SM Mayanna - 1979 - nopr.niscair.res.in

The kinetics of OsO_4,-catalysed oxidation of benzyl alcohol by chloramine-T (CAT) in alkaline solution has been studied. The oxidation follows complex kinetics, the order with respect to chloramine-T, substrate and OsO_4. each being unity.

14. Kinetics and mechanism of osmium (VIII)-catalysed and uncatalysed oxidation of aminoalcohols by chloramine-T in alkaline medium

S Gupta, V Ali, SK Upadhyay - Transition Metal Chemistry, 1988

The oxidation rate is directly proportional to [osmium(VIII)] in primary amino-alcohols, while that is proportional to {k′+k″ [osmium(VIII)]} (where k′ and k″ are rate constants) in diethanolamine and triethanolamine.

15. Osmium (VIII)-catalysed Reactions of Allyl & Crotyl Alcohols with Chloramine-T, Chloramine-B, Bromamine-T & Bromamine-B: Kinetics & Mechanism of …

HMK Naidu, B Yamuna, DS Mahadevappa –jics 1987

16. Kinetics and mechanism of the oxidation of phosphite with chloramine T catalyzed by osmium (VIII) in alkaline solutions

L Bhatt, PD Sharma, YK Gupta - Journal of the Chemical Society …, 1984

17 **Oxidations of Organic Compounds with Osmium Tetroxide**

. Organic Syes by Oxidation with Metal Compounds pp 633-693| Cite as

Metal compounds like potassium permanganate, hexacyanoferrate(III), ruthenium tetroxide, and osmium tetroxide are widely employed as oxidants in an alkaline medium. Apart from synthetic applications in the laboratory these oxidants are also important in industrial syntheses. Osmium tetroxide is the oldest compound and has been generally used for hydroxylation of olefins.

18. Kinetics and Mechanism of Osmium(VIII) Catalyzed Oxidation of Uric Acid with *N*-Chloro-*p*-toluenesulfonamide (Chloramine-T) in Alkaline Medium

Sharma Nidhi [1] , Mishra Som Kant [1] , Sharma Prem Dutt

Bulletin of the Chemical Society of Japan 1992, Vol.65, No.4 1125-1130

Osmium(VIII) catalyzes the reaction intramolecularly via redox cycle of Os(VIII)/Os(VI).

19. Os(VIII)-catalyzed mechanistic investigation of oxidation of some benzimidazoles by chloramine-T in alkaline medium

Ramalingaiah [a]R.V.Jagadeesh [b]Puttaswamy

Catalysis Communications

Volume 9, Issue 6, 31 March 2008, Pages 1443-1452

the oxidation reactions follow identical kinetics for all the five benzimidazoles with first order dependence each on $[CAT]_0$ and $[substrate]_0$ and fractional order dependence each on $[OH^-]$ and [Os(VIII)]

20. Os (VIII) Catalysed Oxidation of Schiff Base by Chloramine – T in Aqueous Acetic acid medium – Kinetic study of the effect of Substrate S.Rosy Christy1 , Dr.V.Krishnasamy
Int.l J of Innovative Res. in Science, Engineering and Technology Vol. 2, Issue 3, March 2013
The kinetic study of simple and substituted anils ware studied under various conditions viz., solvent ,oxidants , electrolyte , catalysts and mixture of catalysts and temperature; simple and substituted anils , pyridinium Chloro Chromate(PCC) ,Pyridinium Dichromate (PDC) were prepared in the laboratory and kinetic study were carried out using oxidant , substrate , solvent and catalyst

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6. Cotton, F. A. (2007). *Advanced Inorganic Chemistry* (6th ed.). New Delhi, India: J. Wiley.
7. Refrences of research papers are given simultaneously.

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