PHYSICO-CHEMICAL STUDIES OF THE DEGRADATION OF THE SURFACTANTS AND BIOINORGANIC COMPOUNDS

An ABSTRACT

of

THESIS

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ABSTRACT

The mechanism of a chemical reaction cannot be fully described without the determination of its rate. The kinetic study of a wide range of chemical processes is seen to be of essential importance, not only in pure research but increasingly in industrial research, development and, in some instances, in quality control and analysis as well. Kinetic methods have become an essential technique in photochemistry, enzyme chemistry, study of chemical catalysis *etc.*

The study of oxidation of organic compounds is of immense importance both from mechanistic and synthetic points of view. It has a bearing on the chemical processes of life also. Investigation of the kinetics and mechanism of redox reactions has attracted the attention of chemists world over and mechanisms of several reactions have been clearly delineated.

The influence of organized media (micelles, vesicles, membranes, *etc.*) on the course of a large variety of chemical and biochemical reactions is now well documented. Ionic micelles typically increase rates of reactions of reactive counter ions with hydrophobic substrates that bind to micelles. These rate increases are due to higher local concentrations of both reactants at the micelle- water interface as compared to their stoichiometric concentrations.

Surfactants are referred as amphiphilic, amphipathic, heteropolar or polar/non-polar compounds, as they possess distinct regions of hydrophobic (water repelling) and hydrophilic (water loving) character in their molecules. The utilization of surfactants as reaction media affects rates, products, and in some

cases, stereochemistry of the reactions. Mechanistic work on micellar effects is typically done using reactant concentrations much below those required fornormal preparative work. Micellar solutions in some cases have proved superior to organic solvents as reaction media to obtain better yield. Evidence is now accumulating which indicate that studies of chemical reactions in micellar media could provide an understanding about the reactions, which take place at the interface.

Electron-transfer processes in micellar systems can be considered as models to get insight into electron-transport occurring in biological phenomena. It has been established that arrangement of hydroxy groups in polyhydroxylic molecules affect the oxidation rate of chromium (VI). There have been only a limited number of studies of chromium(VI) redox reactions in surfactant media. Therefore, we have made systematic studies of the oxidative degradation of surfactants by different oxidant metal-ions. Kinetic studies are expected to provide information on how the electron-transfer event is affected by hydrophobic and electrostatic interactions between the micelles.

The work in this thesis has been divided into three chapters, namely,

(i) Chapter 1- General introduction;

(ii) Chapter 2- Experimental;

(iii) Chapter 3- Results and discussion.

Chapter –1: Comprises of an introduction of degradation of surfactants and bioinorganic mlecules, metal ion oxidation of organic substrates and statement of the problem.

Chapter-2: Contains experimental details. The source and purity of various reactants and surfactants are mentioned in this chapter (Table 1). Procedures for the preparation of the solutions, kinetic measurements and viscosity measurements under the reactions conditions have been detailed.

Different experimental conditions were adopted by varying the concentrations of oxidant metal ions [chromium (VI), cerium (IV), permanganate], surfactants [(EDTA), (TritonX-100), (SDS)], biomolecules [lactic acid and D-fructose] and salts [$Na_4P_2O_7.10H_2O$, NaF, $MnCl_2$, $H_2C{=}CHCONH_2$] to elaborate their possible roles in the oxidative degradations.

Chapter- 3: This chapter has been sub- divided into six parts, namely,

A. Kinetics and mechanism of oxidation of EDTA by chromium(VI) in presence of perchloric acid.

B. Kinetics and mechanism of the oxidation of lactic acid by chromium(VI) in presence ethylenediaminetetraacetic acid, 2, 2$^{'}$bipyridyl, and manganese(II).

C. Kinetics and mechanism of oxidation of Triton X-100 by cerium(IV) in presence of sulfuric acid.

D. Kinetics and mechanism of oxidation of D- fructose by cerium(IV) in presence of H_2SO_4

E. Kinetics and mechanism of oxidation of sodiumdodecyl sulphate by Permanganate in presence of perchloric acid

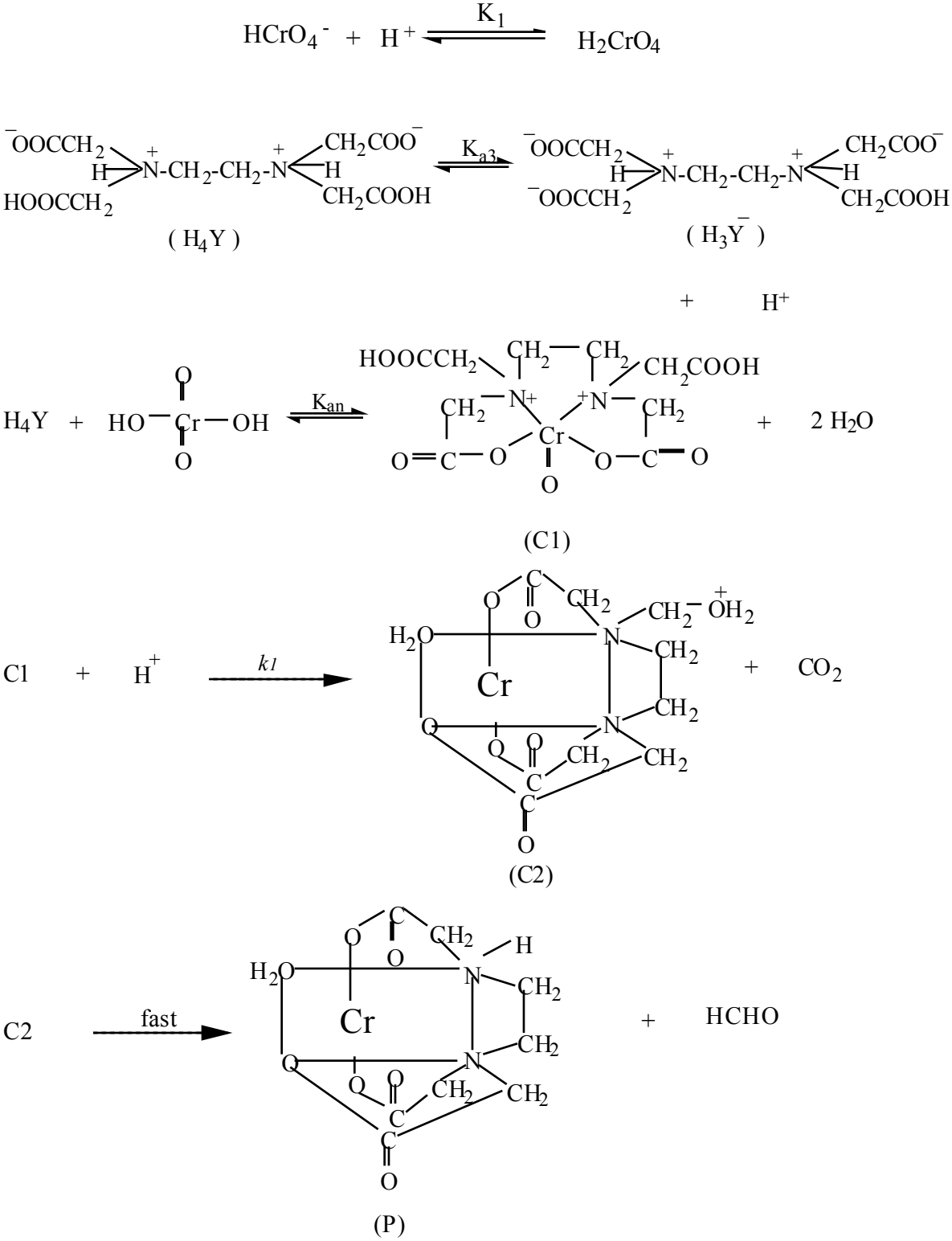
F. Kinetics, mechanism and cloud point of TritonX-100 by permanganate in presence of perchloric acid

The values of the rate constants were found to be independent of the initial concentration of chromium(VI) [EDTA, lactic acid], cerium(IV) [TX-100, D-fructose] and permanganate [SDS, TX-100] showing a first-order dependence of rate on [oxidant].

The redox reaction between chromium(VI) and EDTA shows a first order dependence on[EDTA] while for the reaction between chromium(VI) and lactic acid the order lies between one and two. The reaction between TX-100 and cerium(IV) shows first- and zero- order at lower and higher [TX-100],respectively while for cerium and D-fructose the order with respect to [D-fructose] is one. In case of redox reaction between SDS and permanganate the order lies between one and two for [SDS] and is first order for [TX-100].

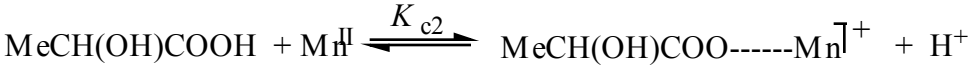
The mechanisms, which account for all the experimental data for the redox reactions between chromium(VI)and EDTA, chromium(VI) and lactic acid, cerium(IV) and TX-100, cerium(IV) and D-fructose, permanganate and SDS and permanganate and TX-100 are given in the schemes 1-6 respectively.

Mechanism for chromium(VI) and EDTA

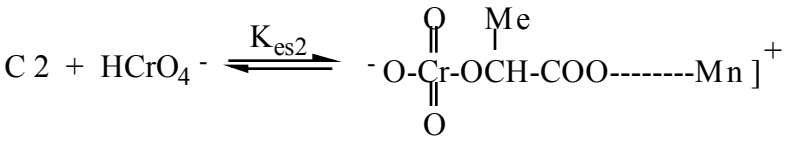


Scheme 1

Mechanism for chromium(VI) and lactic acid



C 2

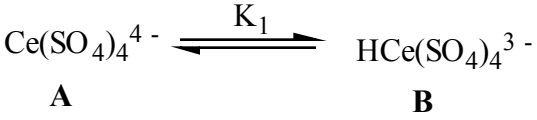


C' 2

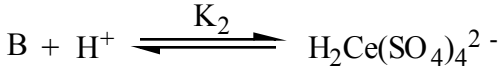
P 2 **P 3**

Scheme 2

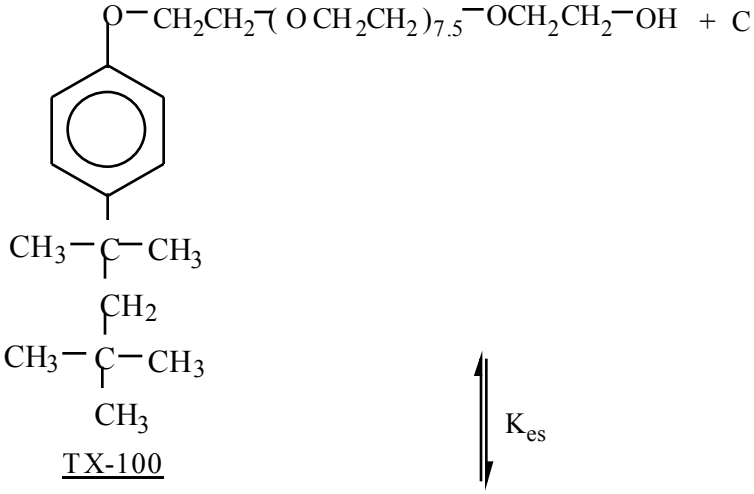
Mechanism for cerium(IV) andTX-100

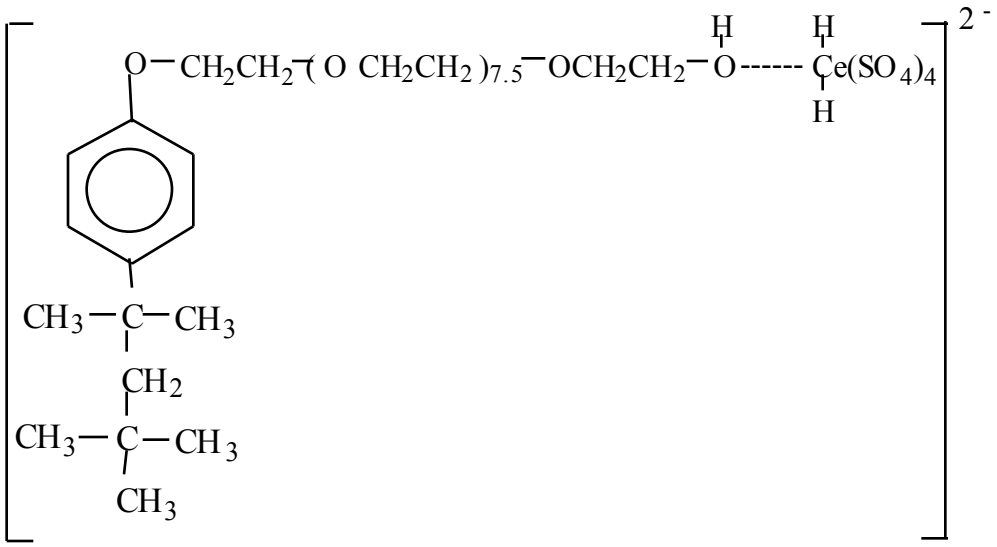


A **B**

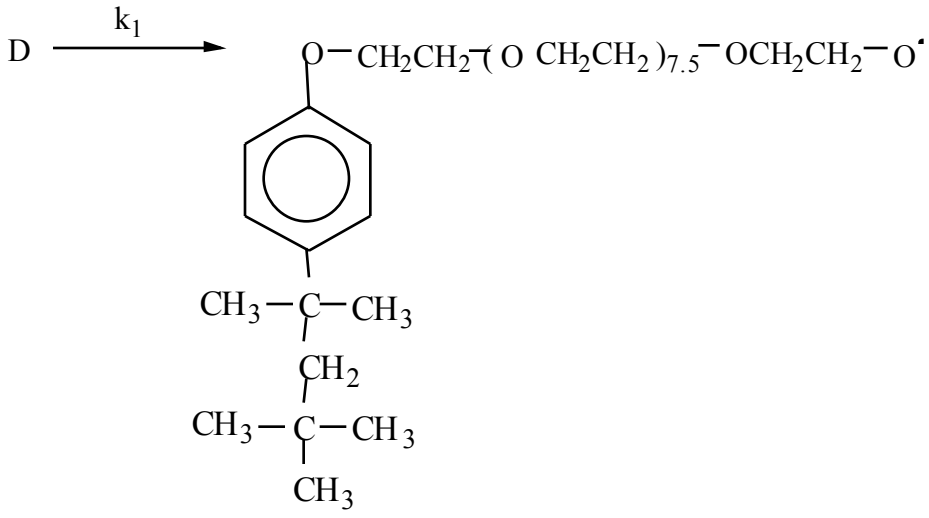


C

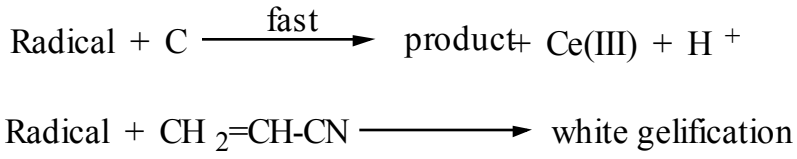


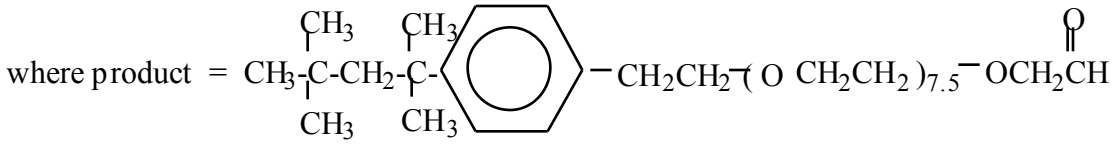


D



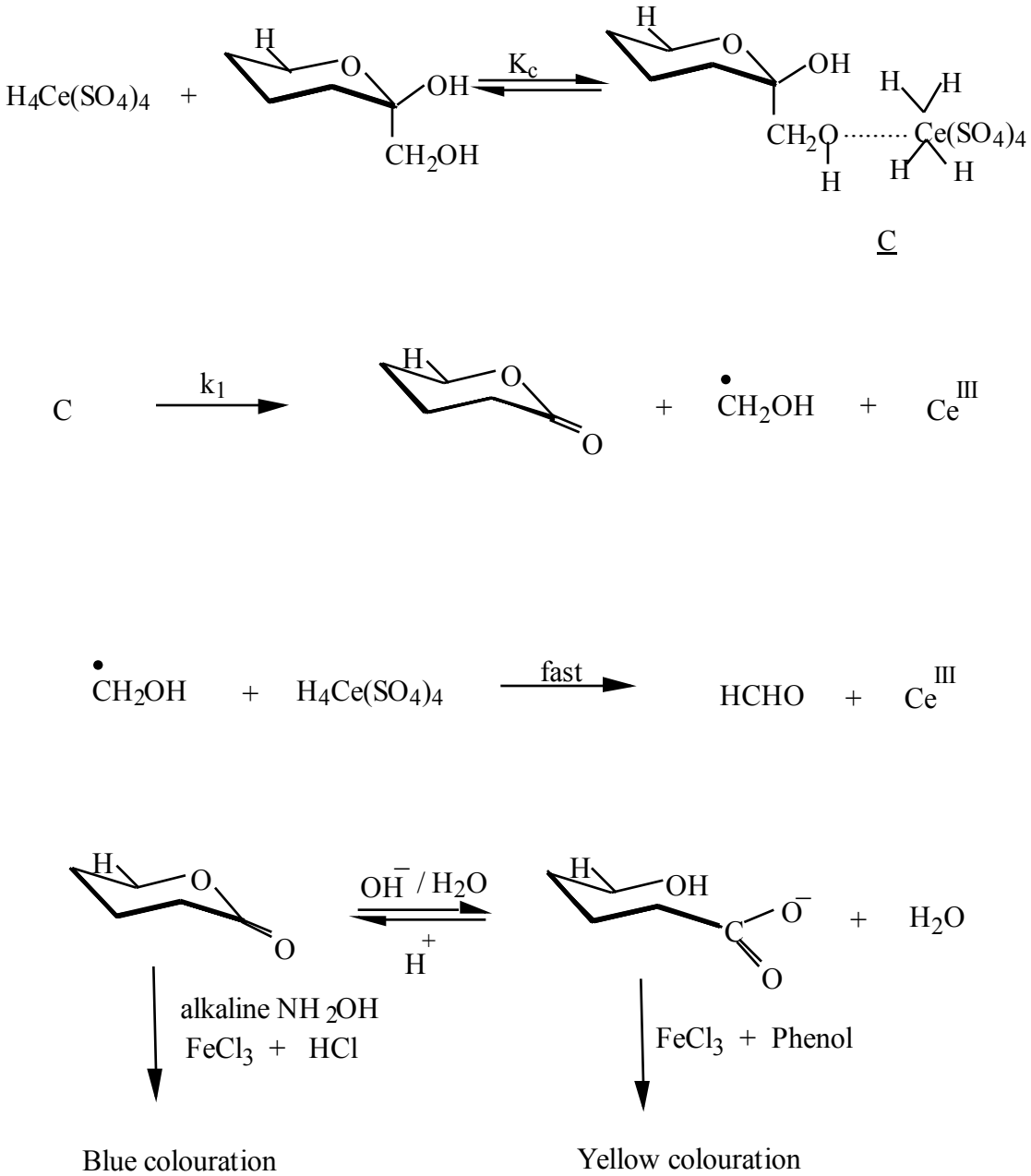
Radical





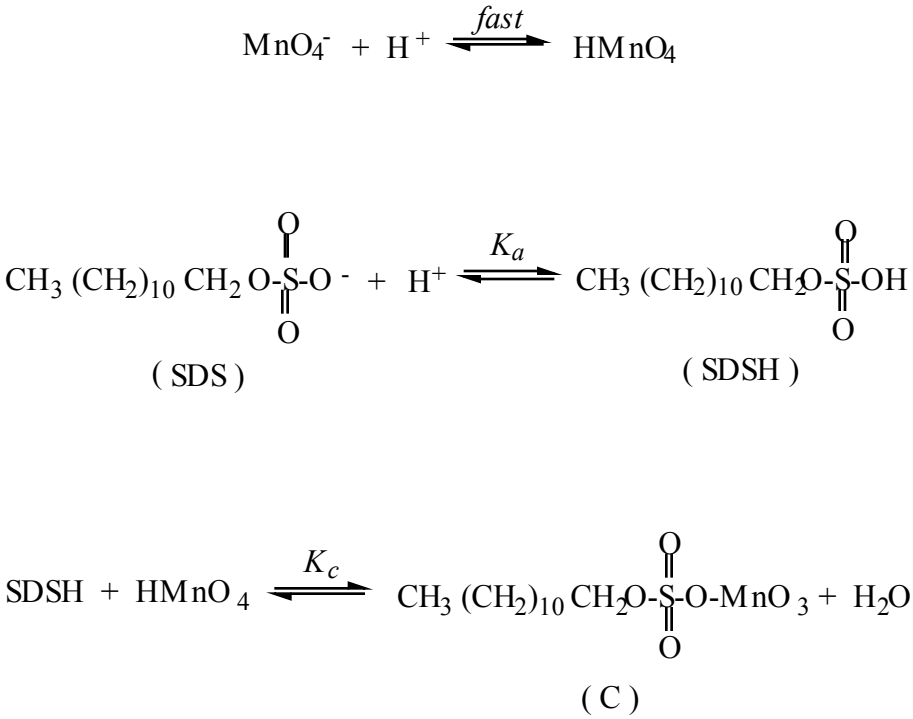
Scheme 3

Mechanism for cerium(IV) and D-fructose



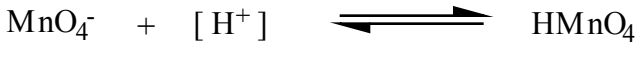
Scheme 4

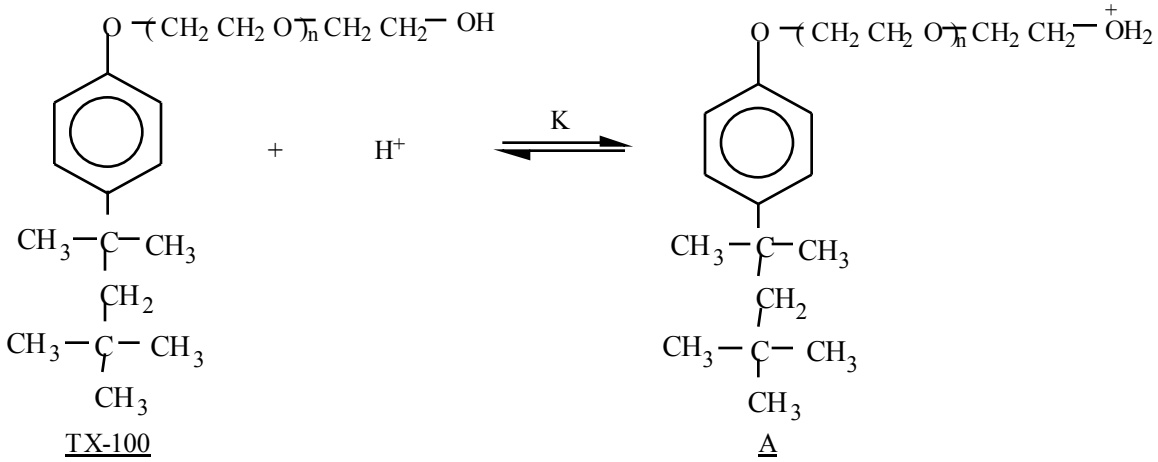
Mechanism for permanganate and SDS

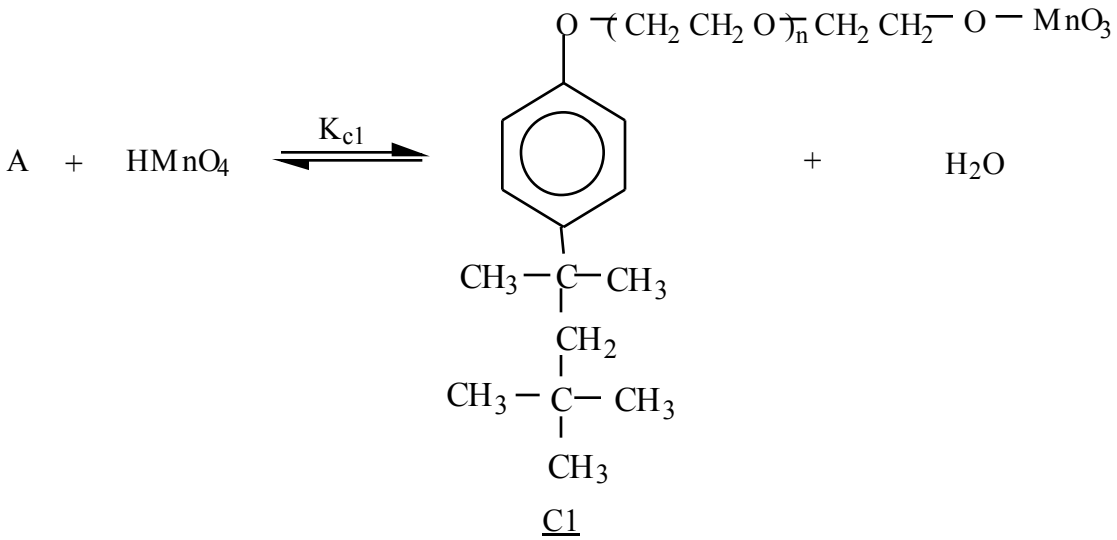


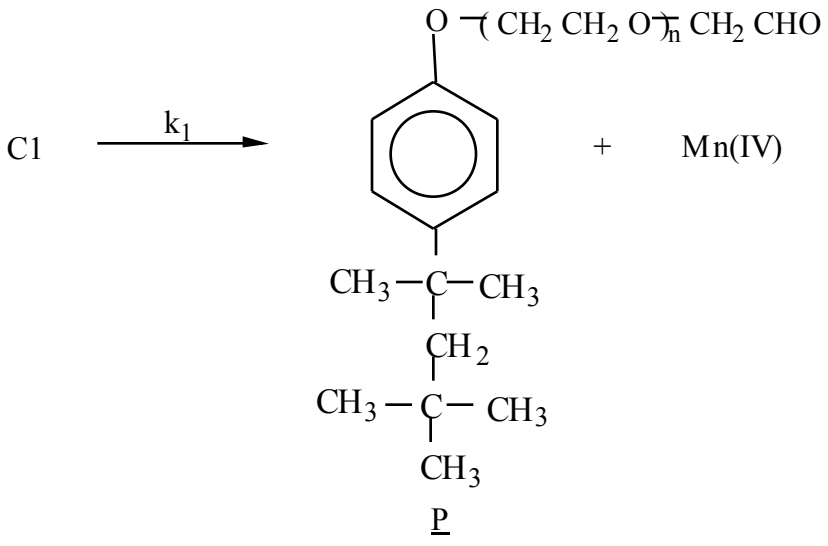
Scheme 5

Mechanism for permanganate and TX-100









Scheme 6

Surfactant monomers rapidly join and leave micelles and the aggregation number represents only an average over time. Micelles are not fixed entities but havea transient character. According to the multiple equilibrium models, therefore, the distribution of surfactant (D_1) between various states of aggregation is controlledby a series of dynamic association- dissociation equilibria.

$$D_1 + D_1 \rightleftharpoons D_2$$

$$D_2 + D_1 \rightleftharpoons D_3$$

$$D_{n-1} + D_1 \rightleftharpoons D_n$$

The small aggregates of the surfactant (dimmers, trimers, tetramers, etc) exist below the cmc. These small submicellar aggregates are responsible for the oxidation of SDS and TX-100 by MnO_4^- and TX-100 by cerium(IV). The equilibrium between the micelles and sub-micellar aggregates is fast. In presence of oxidant, the equilibrium shifts towards the right-hand side because monomeric surfactant is consumed and is oxidized to product. On the other hand, in the micellar pseudo phase the aggregated surfactant molecules (D_n) are oxidized by the oxidant.