

## Kinetics Of Oxidation By Using Polyoxometalates

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The most intriguing chemistry branch which deals with the study of reaction rate is termed as Chemical kinetics. Thermodynamics is a chemistry branch which deals with the feasibility of a reaction. Any chemical reaction has thermodynamic and kinetic aspects. Kinetics is related to reactivity and thermodynamics is related to stability. Chemical kinetics provides a wealth of recognition of both practical and fundamental interest. There are numerous organic and inorganic reactions that can be studied under chemical kinetics. There are numerous organic and inorganic reactions that can be studied under chemical kinetics. Some reactions completed at very high speed, within fraction of second, while some reactions are extremely leised. Iron rusting in the presence of air and moisture is reported to be very slow. In the midst of them there are some reactions consuming moderate time for completion that can be studied conveniently with suitable methods. Kinetics is perturbed with the quantitative knowledge of the reaction rate and of the factors upon which the rate depend, prediction of a time-dependent system and the plausible mechanism by which reaction undergo procession. Kinetics provides an account to understand the optimum conditions for the reaction to enhance the maximum yield of product. The first kinetic measurement was carried out by German chemist Ludwig F. Wilhemy[1] in 1850 by using polarimeter. Wilhemy measured the rate of inversion of sucrose and reported that the reaction rate depends on the first power of the sucrose concentration. Since then the most powerful tool for determination of reaction mechanism is to follow the reaction kinetics. With the growing realization of the challenges in the assay compounds of Medical and biological importance, the kinetic methods of analysis are highly sensitive, selective, simple, accurate and less expensive. Harcourt and Esson [2-3] performed the reaction between potassium permanganate and oxalic acid and investigated an expression for the amount of

reaction as a function of time for a “first-order” reaction in which the rate is proportional to the concentration of one reactant only. Berthelot and S T Gilles [4-5] reported acquisition of the rate of esterification of ethanol and acetic acid. The rate depends on the product of both the reactants concentration. For a “second-order” reaction, the velocity is proportional to the concentration of two reactants (substrate).

According to the Law of mass action, the velocity of reaction depends on the active masses of the reacting substrates at any given instant. The active masses of the reacting substrates decrease with time; hence the reaction proceeds rapidly at first but slows down with time. This indicates that the reaction rates cannot be obtained by simply dividing the number of moles reacted by the corresponding time interval but it has to be actually evaluated at the desired instant. Kinetics is a tool to acquire knowledge of reaction mechanism and to get detailed information regarding nature and course of the reaction. To understand the mechanism of any reaction chemist must know a reaction as a function of time. Kinetics provides a framework for designing experiments. It covers empirical studies of the effect of various factors such as concentration, stoichiometry of the reaction, estimation of the product, effect of substituent on the reaction rate, temperature, solvent medium, hydrostatic pressure of the reaction system etc. and mechanism. Kinetics study plays major contribution to the reaction mechanism elucidation.

For the reaction in solution, the mechanism is framed on the basis of different kinetic parameters. Apart from the order of reaction, effect of concentration of catalyst (if any), temperature, salt effect, solvent etc. on velocity of reaction also provide valuable information so as to suggest the most probable mechanism of the reaction. Further, the isolation of the intermediate and identification of their structure and the use of isotopic methods have

also proved to be a major contributing factor in elucidating possible reaction mechanism.

Kinetics knowledge helps in predicting transformation of the reactant molecules into the product and the time scale for the transformation, determination of the yield of the products, relative reactivity of the molecule and also the feasibility of the particular reaction under particular conditions. During a chemical reaction, there is a change in concentration of the reacting substances. These concentration changes would decrease with the passage of time and after a particular period of time, the concentration becomes time independent. This state of the system when the properties of the system become time independent is referred to as the equilibrium state. Guldberg and Waage[6] noticed that the law at chemical equilibrium can be applied to the kinetic rate laws by assuming that at equilibrium, the rate of forward and reverse reaction are equal. Chemical kinetics offers a technique for examining the manner in which molecules, ions etc. take part in chemical reactions. It helps us to understand the mechanism of the chemical reaction. It is said that "Mechanism is to chemistry as a grammar is to a language; there is no branch of chemistry which can be satisfactorily studied without clear grasp of the principles of the mechanism." A Reaction mechanism is termed as the sequence of elementary steps that accomplishes the reaction. Thus, reaction mechanism focuses on the various steps occurring during reaction course and also focuses on the intermediates.

#### Importance of chemical kinetics in reaction mechanism:

The study of chemical kinetics is of wide significance in the physiological processes, reaction design, electrode processes, reaction mechanism, the study of drug action etc. indicates its importance. Chemical kinetics also plays an important role in photochemistry, electrochemistry, biochemistry, radiation chemistry and catalysis.

During the course of a chemical reaction, molecules come closer, atoms change their positions, electron shift takes place and as a result, new compounds are formed. The reaction may include a series of small changes sequentially. Reaction mechanism helps in describing one or more steps taking place in the sense of how various bonds are

broken and made during the course of reaction. For the recognition and prediction of experimental results researchers mainly use mechanistic tool for most of the reactions. A reaction mechanism is only one of many models used by the scientists to try to understand and predict experimental results. The elaboration of step-by-step paths of conversion of reactants into products is called reaction mechanism. In reactions that proceed by series of step, the slowest step is recognized as the rate determining step. Once it is completed the subsequent steps occurs at a quite faster rate than the slowest step. The overall rate of the reaction is governed by the rate of the slowest step. Chemical kinetics covers a very wide area including empirical studies of the effect of various factors responsible for elucidating mechanism. The rate equation and order of reaction together are used to deduce the reaction mechanism.

#### Rate or velocity of Reaction:

To determine the mathematical form of the rate law and to measure the reactivity of substrate rate measurement is essential. Reaction rate reported to be dependent on the substrate concentrations and on the temperature of the reaction mixture. The bread and butter of chemical kinetics is the measurement of the rates of chemical reactions. Rate of reaction is defined as, the alteration in number of reactant molecules of per unit time". It is also defined as "the change in concentration of reactant (or product) in a unit interval of time". The representation of reaction rate in terms of concentration of the reactants is emphasized as rate law. The rate law provides insights into the series of elementary steps taking place during reaction course.

$$\text{Rate of reaction} = -dc / dt \text{ ----- (1)}$$

Where, 'c' is substrate concentration at corresponding time 't'

The negative sign in rate law equation emphasizes that the [reactant] decreases with the time. On the contrary, the rate with respect to product having concentration 'x' at any time 't' is given by

$$\text{Rate of reaction} = \frac{dx}{dt} \text{ ----- (2)}$$

The positive sign emphasizes that the [product] increases with time. Thus in short, an expression which shows a dependence of rate on concentration of reactant is called the rate law or rate equation,

$$\frac{-dc}{dt} = \frac{dx}{dt}$$

The rate equation cannot be deduced from the stoichiometric equation. The rate law for a reaction must be determined by experimental technique. Rate equation may not include all the reactants written in balanced equation. At a fixed temperature, the rate of reaction depends on concentration of reactant for a given reaction.

$$\text{Rate} \propto [A]^n$$

$$\text{Hence, Rate} = k [A]^n$$

The proportionality constant 'k' is called rate constant. The value of 'k' depends on rate equation and order of the reaction.

Knowledge of rate law allows us to predict the rates of reaction for new values of the concentrations without doing additional experiments. Rate law provides information about the sequence of molecular steps that constitute the reaction.

For the reaction in solution, the mechanism is based on different kinetic parameters in which order of the reaction with respect to the different reactants is most important. Apart from an order of reaction, the factors, which affect the rate of reaction are, nature of the reactants, physical state, concentration, temperature, catalyst (if any), salt effect, solvent etc. and provide valuable information so as to suggest the most probable mechanism of the reaction.

**A] Concentration:** Ionic compounds have a tendency to undergo change rapidly than covalent compounds. A large surface area of reactant is helpful in increasing the reaction rate. In collision theory, it is anticipated that the rate depends on the collision frequency, the fraction of collisions that occurs with the least kinetic energy  $E_a$  along their lines of centers, and also depend on a steric factor. For the determination of reaction rate at constant volume, the concentration of a chosen reactant or product is determined at various time intervals. The rate of change in concentration of the reactant ( $\Delta C$ ) for given time interval ( $\Delta t$ ) is obtained by calculating  $\Delta C / \Delta t$  Hence reaction rate has unit  $\text{mol lit}^{-1} \text{sec}^{-1}$  for zero-order reaction. In general reaction rate has unit  $\text{time}^{-1} (\text{Concentration})^{1-n}$ .

Concentration plays significant role in elucidating reaction rate. Rate of reaction and concentration of the reactants are mathematically

related by rate equation. At initial stage, the reaction rate is faster. The rate started dropping as concentration of reactant decreases. According to the collision theory of chemical reaction, the reactant molecules must collide in order to react together. As the concentration of the reactant increases, the frequency of the molecules colliding increases, striking each other faster by being in closer contact of any given point in time. Thus the increase in the concentration of the reactant increases the number of particles in a given volume, thereby increasing the effective collision rate of the molecule. The higher frequency of collisions results in a higher rate of reaction.

**B] Temperature:** A velocity of a chemical reaction and rate coefficient both depends on the temperature (T). In homogeneous reactions, the rate of reaction becomes doubled or tripled for each  $10^\circ\text{C}$  rise in temperature. In 1878, J. J. Hood [7] was the first who investigated that with the rise in temperature, the reaction rate increases. Hood suggested an equation to give a relation of rate constant (k) with absolute temperature.

$$\ln k = A - B / T \dots\dots\dots[\text{I}]$$

Where, A and B are constants for the reaction system. The value of A and B may be obtained from the intercept and slope of a linear plot between  $\ln k$  and  $1/T$ . In 1884, some theoretical significance to this law was given by Van't Hoff, who argued on the basis of the effect of temperature on equilibrium constants [8]. Arrhenius successfully applied his ideas to the experimental data for numerous reactions. He suggested an equation to show the variation of rate constant (k) of reaction with absolute temperature (T) in 1889.

The Arrhenius equation in its integrated form is,

$$k = A e^{-E_a / RT} \dots\dots\dots[\text{II}]$$

Where, k is Rate constant of reaction, A is Arrhenius factor,  $E_a$  is Activation Energy and, R is Gas constant

To account for the marked increase in reaction rate with the rise in temperature, Arrhenius suggested that, molecules absorb heat energy and get activated. According to his hypothesis every system in equilibrium exists between normal reactant molecules and activated molecules. This is related to the fact that each particle (molecule, radical, ion) is a rather stable structure. Its rearrangement requires a

weakening of certain bonds, which needs energy consumption. This energy, necessary for the chemical transformation of the reactants, is named the activation energy. Thus molecule acquires the additional energy required for a reaction to occur, which is known as the activation energy. A low value of  $E_a$  and  $\Delta H^\ddagger$  suggest fast reaction rate, whereas high value suggests a slow rate of reaction. In the vicinity of room temperature RT is about 600 cal. Thus there is relatively very little difference between activation energy ( $E_a$ ) and  $\Delta H^\ddagger$  and these values are frequently used interchangeably in the literature to define the activation barrier of a reaction.

Entropy is a thermodynamic property that is a measure of randomness or disorder of the molecules of the system. It is a state function. In 1850, Clausius introduced a numerical definition of entropy.

$$\Delta S = \frac{q}{T}$$

According to Clausius, entropy of system is a constant quantity when there is no communication of heat. SI unit of entropy is  $\text{J mol}^{-1}\text{K}^{-1}$ .  $\Delta S^\ddagger$  has the CGS units of calories per degree per mole, sometimes it is referred to as entropy unit 'eu' or in the new usage as Gibb's per mole [8]. To calculate entropy change,  $\Delta S^\ddagger$  by equation, one inserts a good experimental rate constant, the corresponding absolute temperature and  $E_a$ , the Arrhenius activation energy calculated as described above[9]. The rate of reaction is a function of the activation energy which represents the energy necessary to get reactants to the transition state.

The enthalpy of activation can be calculated with equal validity from, the pseudo-first order or second-order rate constants for a reaction. This is because it is derived from the rate of change with temperature and not from absolute values of rate constants. Generally various values of  $\Delta S^\ddagger$  is calculated from, the pseudo-first-order rate constant for a reaction than from second order rate constant for the same reaction. The rate constant used for calculation of  $\Delta S^\ddagger$  should pertain to the correct rate law as determined experimentally.

The positive values for the entropy of activation indicate that the transition state is highly disordered compared to ground state which leads to a fast reaction rate. It is beneficial for the kinetic

researchers to observe the amount of change in  $\Delta H^\ddagger$ , and in  $\Delta S^\ddagger$  that bring about ten-fold change in reaction rate.

**C) Catalysts:** In 1836, Berzelius defined a catalyst as a substance which alters the rate of chemical reaction and itself remains chemically and quantitatively unchanged at the end of the reaction. Earlier, it was thought that a catalyst does not appear into the stoichiometric equation of chemical reactions. A catalyst generally provides an alternative mechanism involving that compete with the uncatalyzed mechanism. The successful exploration of catalyst will provide value added products with improved yield which help in eliminating or minimizing environmental pollutants.

**Types of catalysis:** Depending on the phase of reactants and products the process of catalysis has two types.

**Homogeneous catalysis:** The reaction in which reactant, product and catalyst are in the same phase is called homogeneous catalysis and the catalyst is called a homogeneous catalyst. For example the inversion of sucrose, the mutarotation of glucose in presence of acids and bases and reaction of tartarate ions with hydrogen peroxide solution to form malonate ions in the presence of cobalt ion catalyst. Enzyme catalysis is a special class of homogeneous catalysis. In cellular biological organisms nearly all chemical reactions are catalyzed by enzymes. For example, enzyme urase catalyzes the hydrolysis of urea, whereas, the enzyme protease catalyzes the hydrolysis of protein.

**Heterogeneous catalysis-** The reaction in which reactant, product and catalyst are in the different phases is called heterogeneous catalysis and the catalyst is called a heterogeneous catalyst. In heterogeneous catalyzed reaction, the surface of a solid acts as a catalyst while the substrates are in gaseous or liquid phase. This is analogous to the formation of an intermediate complex in homogeneous catalysis. For example the hydrogenation of  $\text{C}=\text{C}$  in presence of solid catalyst like Pt, Pd, Ni, Cu by using gaseous hydrogen.

Recent developments in the nanotechnology have produced nano-meter size a solid particles that act as efficient catalysts[10]. A solid catalyst acts by adsorbing molecules from a gas or liquid phase onto its surface, where they react. Transition metal

substituted heteropolyoxometalates are reported to have attractive catalytic action due to their diverse chemical and electrochemical properties[11]. In the acid-base and redox reactions Keggin type HPA's are widely applicable as homogeneous and heterogeneous catalyst. Recent interest in POM is mainly centered on Dawson and Keggin species and their acids for their remarkable catalytic property[12].

**E) Salt effect:** The influence of charged species on the rate of reaction is known as salt effect. In the case of an ionic reaction, the reaction rate not only depends upon the nature of the reacting ion but also on the ionic strength of the reaction medium. A very satisfactory treatment of this matter was made by Bronsted[13], Bjerrum[14] and Christiansen [15], and was reviewed later on by Lamer [16].

**D) Dielectric constant:** Dielectric constant is solvents ability to reduce the internal charge of the solvent. The hydrogen atom in a polar protic solvent is reported to be highly positively charged and it can interact with anionic nucleophile which would negatively affect a bimolecular nucleophilic substitution reaction  $SN^2$ . But it does not affect unimolecular nucleophilic substitution reaction  $SN^1$  because nucleophile is not a part of the rate determining [17]. The role of dielectric constant of solvent is important in reactions involving the electrostatic forces between solvent and solute molecules. Amis [18] has explained the subject systematically.

To explain the effect of a dielectric constant of solvent ( $\epsilon$ ) on rate of reaction between two ions having valance  $Z_A$  &  $Z_B$ , Scatchard[20] derived following expression,

$$\ln k = \ln k_0 - Z_A Z_B e^2 / 4 \pi \epsilon_0 \epsilon D_{AB} k_b T$$

Where,  $\epsilon$  is the dielectric constant,  $\epsilon_0$  is permittivity of a vacuum ( $8.854 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$ ),  $k_0$  is the specific rate constant in the hypothetical medium having indefinite dielectric constant  $\epsilon = 0$  And  $e$ ,  $K_b$ ,  $D_{AB}$ ,  $T$  are referenced as the electronic charge, Boltzman constant, radius of activated complex and absolute temperature respectively.

The above equation implies that logarithm of the rate constant of ionic reaction varies linearly with the reciprocal of dielectric constant ( $\epsilon$ ) by the solvent.

### Kinetics of Electron-Transfer (Redox) Reactions:

Numerous organic and inorganic reactions studied kinetically like oxidation–reduction, hydrolysis, photochemical reactions, displacement, addition, substitution etc. which find application in various fields. Among them, redox reactions are recently studied widely and are called electron transfer reactions.

The interest in redox reaction has been renewed due to their application in catalysis and synthetic organic chemistry. The classical definition of oxidation and reduction in terms of gain or loss of oxygen has in modern times been abandoned in favor of the concept of electron loss(oxidation) and electron gain (reduction). Redox reactions can also be defined in the form of changes in oxidation states or oxidation numbers. The change in oxidation number indicates the existence of a redox reaction. A comparison of oxidation states of atoms in reactant and product enables us to keep a track of the transfer of electrons in a chemical reaction

**POLYOXOMETALATE(POM):**-POM structure may be defined in general terms as molecular metal oxide clusters formed through a condensation reaction of early transition metal-oxygen anions. The early transition metals in group 5 and 6 of the periodic table, usually with the metal centers in their higher oxidation states are preferred for POM synthesis. The majority of POM structures currently studied are composed of aggregations of molybdenum or tungsten or less abundantly vanadium oxoanions. POM represents a large class of coordination compounds widely used in various areas of science and technology. Since POM's have a unique structure and physicochemical properties, they are used as homogeneous and heterogeneous catalysts [19-22] and model structures in coordination chemistry[22]. POM's have a compact size and shape with a remarkable degree of tunability which made them useful probes of fundamental structures and dynamic issues in chemistry and practically useful entities.

**Catalysis by Polyoxometalates:-** POM anions are ideal candidates for the study of homogeneous outer-sphere electron-transfer redox reactions. Early POM's are large and rapidly growing class of HPA's or heteropoly salt. The first report of POM by Berzelius back in 1826 opened the many applications

of heteropolyacids in the field like material sciences, structural biology, medicine, and catalysis. POMs have several advantages as a catalyst and oxidant which make them economically and environmentally attractive. There are numerous application of POM's catalysis[23-25]. POM's are also useful for the clean synthesis of fine and specialty chemicals, consequently, much current research is centered on various aspects of catalysis by HPAs[26].

Due to the following properties POM's act as catalyst-

- POM bears different chemical and electrochemical properties.
- They exhibit high structural mobility and multi-functionality.
- Show very strong Bronsted acidity.
- Their acid base and redox properties can be varied over a wide range by changing the chemical composition.
- Discrete ionic structural units as HPAs and counter cations, unlike the network structure of zeolite, metal alkoxide etc. The structure is frequently preserved upon it manifests itself to reveal extremely high proton mobility and a "pseudo-liquid phase".
- POM's are the promising acid, redox and bifunctional (acid/ redox) catalysts, as they have high thermal stability in solid state and high solubility in a polar solvent.
- The catalytic reaction can be performed in homogeneous as well as heterogeneous (gas-solid), liquid-solid and biphasic (liquid-liquid) systems.
- POM's are often used as model systems for fundamental research providing a unique opportunity for mechanistic studies at molecular level. At the same time, they have become increasingly important for applied catalysis.
- Efficient oxidants, exhibiting fast, reversible multi-electron redox transformations under very mild conditions.

The POM's anions are ideal candidates for the study of homogeneous outer sphere electron transfer redox reactions. Charge density is considerably lower in case of isopoly and heteropolymetalates than those found in traditional anions like  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ , which make complexes of transition metal ions with

polyoxoanions like polytungstates to acts as outer-sphere electron transfer reagents. In solid state, POM compounds are supposed to composed of polyoxoanions, cations such as protons, metals and water of crystallization. Sometimes, in addition, they contain neutral organic molecules.

The applications of POM's are centered primarily on their redox properties, photochemical response, ionic charge, conductivity and ionic weights. Literature survey concluded that the majority of the applications of POM's are found in the area of the catalysis. The remaining application includes coating, membranes or thin films. These include corrosion, resistant and in conductive and non-conductive polymers membranes and POM's as surface modifiers of the substrate. POM's are also used as pigments, toners, wood pulp bleaching agent, the reagent for chemical and biochemical analysis and for nuclear waste processing and some miscellaneous applications. The POM compounds are active as oxidation-reduction catalysts with a wide range of organic/inorganic substrates and mostly provide higher activities and selectivity and allow for cleaner processing compared to conventional catalysts. The use of a variety of multi-component redox systems based on POM's greatly enhances the scope of possible oxidations.

**AJ Oxidation of Inorganic and Organic substrate by POM anion as efficient Oxidant:-** The survey of the literature showed that oxidation of various inorganic or organic substrates was studied kinetically by using POM as oxidant [27-46] and as a catalyst under mild conditions. POM anions have been used as well-defined outer sphere electron transfer agents. The Keggin structure of 12-tungstocobaltate(III) anion is substitution inert and precluded inner sphere mechanism because the central  $\text{Co}^{\text{III}}$  atom is protected by a sheath of chemically inert oxygen atoms. Electron exchange between the  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{II}}$  compounds in solution is relatively rapid which support outer-sphere electron transfer. In comparison with Keggin and Dawson types of salts, 6-molybdocobaltate(III) salts are substitution inert and are compact. It belongs to Anderson-Evans structure and contains six non-ionisable proton. To the best of our knowledge, very limited study is available on kinetic and mechanistic

study of oxidation by 6-molybdocobaltate(III) anion[45-47].

**B] Oxidation of Inorganic and Organic substrate by using POM anion as catalyst:-** POM's are the promising acid, redox and bifunctional (acid/redox) catalysts, as they have high thermal stability in solid state and high solubility in a polar solvent. Literature survey concluded that the majority of the applications of POM's are found in the area of the catalysis. Carboxylic acid hydrazides are pharmaceutically important organic compounds pertaining anti-tubercular and antibacterial properties. Some POM's like Anderson type Hexamolybdochromate(III) [51,52], 13-Vanadomagnate(IV) [53], Octamolybdomagnate(II) [54], have reported as catalyst for oxidation of hydrazides more effectively than metal ion.

**C] Oxidation of Pharmaceutically Important organic compounds by using POM:-**The study of oxidation mechanism involving drugs was well documented [55-60] in case of 12-Tungstocobaltate(III). While comparatively very few studies are reported on other POM's [61-62]. Recent study focuses on study of electron-transfer processes for pharmaceutical and biological investigations.

#### Conclusion:

POM's have relatively low toxicity as compared to chromates; they accept electrons without major changes of their structures and form insoluble salts with large cations. POM represents thermodynamically stable structural arrangements. They characteristically maintain their identities in aqueous and non-aqueous solution as well as in ionic crystal. These properties make POM attractive as oxidant. The oxidation of organic compounds generally proceeds with very low rates and they require rather drastic conditions. POM show good selectivity and high yields POM's have several advantages as a catalyst and oxidant which make them economically and environmentally attractive.

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