CHEMICAL KINETICS: A DISCIPLINE AND A MECHANISTIC TOOL

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ABSTRACT

The purpose of this review is to introduce young researchers, advance undergraduate and graduate students of inorganic chemistry to the field of chemical kinetics both as a discipline and as a tool in mechanistic diagnosis of inorganic chemical reactions. Inorganic reaction mechanism is an important aspect of inorganic chemistry that deals with the study of the detailed step by step processes through which reactants in chemical reactions are converted to products. The overall equation of a reaction tell us what happens in a chemical reaction, whereas the mechanism explains how it happens –the steps involved and the effect of reaction conditions and catalyst, if employed. The review will deal with concepts and well established principles within the broad fields of chemical kinetics, which can be employed in determining the stoichiometry, kinetics and ultimately the mechanisms of chemical reactions. *[African Journal of Chemical Education—AJCE 9(2), July 2019]*

INTRODUCTION

The review begins with a look at the relevance and application of chemical kinetics before delving into discussion on reaction rate and the techniques for its measurement and interpretations. The results of such measurements show that reaction rates depend on the concentrations of reactants, products and in some cases even intermediates in characteristic manners that can be expressed in terms of differential equations known as rate laws [1]. The rate law describes the effect of concentration on the rate of a reaction and its solutions can be used to predict the concentration of specie at any time after the start of the reaction [2]. The study of reaction rates ultimately leads to an understanding of the mechanisms of reactions [3]. An insight into the elementary steps through which reaction occurs can be gotten from the form of the rate law [1]. Therefore, the main task in kinetics is the construction of a rate law from a proposed mechanism and its comparison with the experimentally determined one [2]. The concepts of the rate determining step of a reaction, the steady–state concentration of a reaction intermediate, and the existence of a pre–equilibrium are all employed in deriving the rate law from the proposed mechanism [4].

The word kinetics has its origin in the Greek word 'kinesis' which means 'to move' or 'moving' [5, 6]. It is a general term referring to time-dependent phenomena that involves change [7]. The principles of kinetics are used in different aspects of sciences [5, 6, 8] and chemical engineering [9, 10]. Knowledge about chemical kinetics is also required for the understanding, design, and control of the chemical reactor, to explain enzyme actions and polymerisation [10], as well as to describe drug degradation and absorption [6]. In fact, nothing is more important in chemistry than the understanding of the mechanism through which chemical reactions occur which explains why kinetics is an important field of chemistry [11].

Chemical kinetics also involves the construction of models that can facilitate the prediction and calculations of experimental results. Modeling and simulation of chemical system can be achieved by a mathematical approach [12]. A model must capture the essentials of a system and the behaviour of a system can be modeled based on the knowledge and dynamics of their components, with the experimental data collected used to obtain kinetics parameters such as rate constant and rate order of a system theoretically. This will then be compared with the experimentally determined ones to confirm the plausibility of a mechanism [12, 13]. Software packages which are based on mathematical models have been designed to simulate reactions and come up with rate data to suggest or validate a mechanism [14]. Recent progress in reaction kinetics can be attributed to the availability of supercomputers and software of quantum chemical methods [15, 16] and the development of methods for monitoring very fast reactions [11, 17].

The significance and importance of kinetics as a field of chemistry is emphasized by the fact that it has produced several Nobel Laureates including Jacobus Henricus van't Hoff, Irvin Langmuir, Manfred Eigen, Henry Taube, Rudolph A. Marcus and Ahmed Zewail [18, 19].

Chemistry is an aspect of science that deals with the transformation of matter [20] and the way and manner through which the transformation occurs is what is refer to as the mechanism of the reaction [21, 22]. These reactions can occur in the gas phase, varying solvents, solid state and at gas–solid or liquid–solid interfaces [10, 23]. Our review is devoted mainly to solution phase chemical kinetics, with emphasis on homogenous reactions taking place in water. The study of homogenous reactions is very important to kineticists since most reactions; from the simple laboratory experiments to the very complex reactions occurring in living systems are homogenous in nature [14].

A thorough study of any chemical reaction should include the study of structures, equilibria and rates [24]. The study of rates of a reaction is under the domain of kinetics. Kinetics can be sub–divided into physical and chemical kinetics. Physical kinetics is concerned with physical phenomena such as diffusion, viscosity and adsorption, while chemical kinetics deals with the study of rates of chemical reactions [25]. Chemical kinetics is a blend of chemistry, physical theory and mathematics, which explains why for a chemistry student/researcher to do well in kinetics, he/she must have a good background in mathematics and a sound understanding of physical theories [2, 11]. The importance of mathematics in kinetics is emphasized by the fact that the law of mass action, which can be said to be the foundation of the modern day rate law, was formulated by a mathematician, Cato Maximilian Guldberg, in collaboration with a chemist, Peter Waage [6]. Also the first Nobel Prize winner in chemistry/kinetics, van't Hoff, was trained as a Mathematician [26].

The reaction that is under study in chemical kinetics is referred to as a system [4, 27], while everything that is not part of the system is called the surrounding [28]. Quite often the surrounding is thermostated water bath that is used to maintain the system at constant temperature [2].

KINETIC STUDY OF A CHEMICAL REACTION

The more one knows about the chemistry of a reaction, the better the conclusions that can be drawn about the mechanism from its kinetic study. Therefore, effective interpretation of kinetic data depends on accurate knowledge of the behavior and occurrence of the reactant species in the solvents in which the reaction will be carried out, the establishment of the stoichiometry of the reaction, the determination and characterization of the products and if possible, intermediate(s) that will be formed during the course of the reaction, and the identification of side reaction(s) [15,

29]. Physical observation, chemical analysis [30], chromatography [31] and spectroscopy [32] can all be used in characterizing the reactants, intermediates and products of a reaction. The method to be employed is determined by the nature of the species under consideration.

The stoichiometry of a reaction is the chemical equation that shows the relative amounts of reactants that take part and the products formed in a chemical reaction [33]. Of the several methods that have been proposed for the determination of the stoichiometry of reactions [34], the Job's method of continuous variation and the Yoe–Jones Molar Ratio methods are the most widely used [35, 36]. A modification of the Yoe–Jones method which is known as the Slope Ratio method, and which involves the addition of measured deficient quantities of one reactant, which is the limiting reagent, to a known excess of the other whose concentration is held constant [35] is also employed by some researchers.

After establishing the stoichiometry of the reaction, characterizing the reactants, intermediates and products of the reaction and identifying any side reactions, the next thing is the determination of the empirical rate law [4]. Rate laws are differential equation that describes the observed rate of reaction in terms of the concentrations of reactants and products in the overall reaction and they are determined empirically [37]. A simple rate equation can be solved analytically using calculus [7]. Complex rate laws can be simplified using the steady-state and equilibrium approximations [24, 38]. They can also be solved numerically using Euler's methods, the midpoint methods, Laplace transform method, Gear method, Matrix method or Runge–Kutta method [39, 40] or stochastically using Monte Carlo [41] or Markov chains [24]. It is often observed that the rate of reaction is proportional to the product of the individual concentrations of the reactants raised to a simple power, known as order of the reaction with respect to those reactants [37].

Since the amounts of products and reactants are related by stoichiometry, any substance in the reaction can be followed and used to express the rate of reaction [17, 37]. Therefore, the basic data of chemical kinetics that is required to come up with the rate law is the concentration of reactant and/or product at intervals after the reaction has been initiated [4]. The method used to monitor the change in concentrations depends on the substance being followed and how rapidly its concentrations changes [15]. The spectral regions have been mostly employed for monitoring the progress of a chemical reaction, with the visible region being the most useful since most reactions of interest involved colored specie [30, 42].

Reactions orders and subsequently rate coefficients can be established the use of differential or integrated equation, isolation (pseudo order) techniques, initial rate method or half–life method [2]. Whatever the experimental method used the reaction must be maintained at a constant temperature throughout [43], except for situations where the experiment is repeated systematically at different temperatures to obtain information on the activation parameters using the Arrhenius [44] or Eyring equation [45].

Once the rate law of a reaction is known and the value of the rate constant determined, the rate of a reaction for any values of reactant concentrations can be calculated [2]. The rate constant for a particular reaction has a fixed value at a particular temperature [46]. The effect of temperature on reaction rate varies considerably from one reaction to another, with collision theory and the transition state theory used for the theoretical explanation of the strong dependence of reaction rates on temperature [2]. According to the transition state theory, the activation energy for a reaction can be lowered by the use of a catalyst [46].

It is generally observed that the rate of reaction can be altered by the nature of the solvent employed [1, 24] and by the presence of non–reacting ionic species in the solution [47]. Since the

rate constants for many reactions are affected by the ionic strength of the medium it is necessary either to maintain a constant ionic strength with added electrolyte [42, 48], or to carry out a series of measurements at different ionic strengths and extrapolate to infinite dilution [1, 15].

INTERPRETATION OF KINETICS DATA

The basic mechanisms of all fundamental elementary reactions include substitution, electron–transfer, insertion, oxidative addition and reductive elimination [4]. Electron–transfer (oxidation–reduction) reactions are perhaps the most important class of inorganic reactions [4, 46]. The study of oxidation–reduction (redox reaction) is important to kineticist because most reactions whether simple or complex, organic or inorganic, chemical or biological, in vitro or in vivo, involve the transfer of at least one electron from a reducing agent to an oxidizing agent [49]. These reactions have been widely studied in an effort to understand the details of their mechanisms [42, 48]. Based on their stoichiometry redox reactions can be classified as complementary or non–complementary, with no direct mechanistic implications [4]. But classification of electron transfer processes as inner-sphere or outer-sphere reactions are based on their mechanisms [37, 42].

A reaction mechanism is a sequence of individual reaction steps, known as elementary reactions or elementary steps, which sum to the overall reaction equation. It is the step–by–step pathway by which a reaction occurs [21]. Mechanisms are the means by which chemical reactions are discovered, rationalized, and optimized. They represent the framework that allows us to understand chemical reactions. General guidelines for proposing plausible reaction mechanism include:

1. The determination of the stoichiometry of the reaction as well as the complete identification of all the reactants and products of the reaction [31].

2. Accumulated data in the chemical kinetics of a related system can be used in comparing, interpreting and analyzing the new experimental data [50].

3. A unimolecular or bimolecular reactions are usually proposed as reasonable steps in a mechanism [25, 27]. Termolecular elementary steps are extremely rare while higher molecularities than three are not known [17].

4. For a mechanism to be plausible, the elementary steps must be reasonable, and must all add up to the overall balance equation of the reaction [17, 46]. Also a mechanism must account for all the kinetic, spectroscopic and theoretical information available on the reaction [17].

5. The form of the experimental rate law provides an insight into the nature of the mechanism of the reaction [4, 17].

6. For reactions in which the magnitude of the stoichiometric coefficient of a reactant is greater than the order of the reaction with respect to that reactant, it means there are intermediate(s) and reactions after the rate determining step [10].

7. If the rate of the reaction is proportional to the concentration of a product raised to a positive exponent, it means the reaction is autocatalytic [23, 38].

8. Once the outline of the mechanism is established, it is necessary to show that the proposed mechanism gives the experimental rate law [51].

9. The polarity and ionic strength of the medium in which a reaction is taking place can both affect the rate of the reaction in a way that can give an idea of the nature of the interactions taking place at the activated complex [24, 47].

10. Interpretation of kinetic data can be made more meaningful by non–kinetic investigations such as the detection of intermediates [10, 13, 52] or radicals [53], or the formation of

isosbestic points [48], or the quantitative analysis of a product [45], which can support or disprove a proposed mechanism.

11. Kinetic isotopic effects give significant information as to the structures of transition states and intermediates and as to the position of bond breakage in the course of a reaction [17, 45, 52].

12. The correlation that exist in the form of linear free energy relationship (LFER) between rate constants and the reactivity of structurally related compounds can be used to diagnose mechanism [54].

13. The effect of added anions and cations give an indication of the type of mechanism operating in a redox process [42, 45].

14. If the proposed rate law from the plausible mechanism does not agree with the experimental rate law even after much modification of the reaction conditions, then the proposed reaction mechanism is rejected and another one proposed.

CONCLUSION

No single review, monograph or textbook can fully cover the broad and important field of chemical kinetics. But we hope our aim of writing a review that can serve as an expository on the principles and methodologies that are employed in kinetics studies and spur researchers' interest in the field by providing a readable introduction to the subject is fulfilled. Elaborate explanations can be found in more advanced and specialized materials on chemical kinetics [7, 9, 23, 37, 55].

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