



Kinetic oxidation of alcohol by N-bromosuccinimide in aqueous acidic medium

Rajendra Prasad Kushwaha¹, Dr. Manju Pandey²

¹ M.Phil. Student, Department of Chemical Sciences, Govt. T.R.S. College, Rewa, Madhya Pradesh, India

² Professor & Head, Department of Chemistry, Govt. T.R.S. College, Rewa, Madhya Pradesh, India

Abstract

The kinetics oxidation of alcohol by N-bromosuccinimide (NBS) in aqueous acidic medium was investigated at 25°C. The influence of the reaction products, ionic strength, temperature effect and dielectric constant of the medium on the rate of reaction was studied. The proposed mechanism is consistent with the observed kinetics. The reaction constants involved in the mechanism were derived. There is a good agreement between the observed and calculated rate constants under different experimental conditions. In fairly high acid concentration, there is no change in the rate of the reaction but at low acid concentration, the rate is considerably enhanced. There is no primary salt effect. At varying mercuric acetate concentrations, the rate constant remains the same.

Keywords: oxidation, alcohol, N-bromosuccinimide

1. Introduction

Chemical kinetics is a branch of chemistry which deals with rate of reaction. A detail study of chemical kinetic along with other non-kinetic study will enable us to understand thoroughly mechanism of reactions. There are some reactions which takes place very fast, within fraction of second (upto femtosecond level). Some reactions are extremely slow for example rusting of iron. In between these two extreme ends, there are reactions which take reasonable time for completion. These reactions can be studied conveniently with suitable methods. There are several researchers who contributed in the field of chemical kinetics. Ludwig Ferdinand Wilhelm, Wilhelm Ostwald, C F Wenzel, Louis Jacques The nard, Pierre Eugene Marcelin Berthelot, Leon Pean de Saint-Gilles, Peter Waage and Harcourt etc. had made pioneering work in the field of chemical kinetics [1-4].

Chemical kinetics covers very wide range. It includes empirical studies of the effect of the concentration, temperature and hydrostatic pressure on reaction of various types. Such studies may be practically important in connection with technical processes. There are different types of chemical reactions and a wide variety of experimental technique has been used to investigate them. A considerable amount of efforts has been taken to study the kinetics and mechanism of the reaction in the gas phase. In many ways these investigations are useful for testing basic theories of reactions. Most of kinetic work has been done on reactions in liquid phase, especially, since it is of greatest interest to the organic and inorganic chemists. A little amount of work has been done on the reaction in the solid phase. The reaction at the gas-solid

interfaces have been received more attention. Though there are various types of reactions, but oxidation reactions are widely studied.

N-bromosuccinimide (NBS) is a source of positive halogen and this reagent has been exploited as oxidant for a variety of substrates in both acidic and alkaline medium [23]. The nature of active oxidizing species and the mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction condition. The species responsible for such oxidizing character may be different depending on the pH of the medium. The probable reactive species [24] of NBS in acid solution are >NX, HOX, > N+HX, or H₂OX⁺ and the reactive species in alkaline solutions are >NH, HOX and OX⁻.

In recent years, studies of oxidation of organic compounds by N-halo compounds in the presence of acid have attracted considerable attention [25]. A thorough literature survey reveals that only few works on the oxidation of 5-oxo acids (S) have been reported [26-27]. Although the N-Bromosuccinimide oxidation of a large variety of organic compounds has been studied, there seems to be no report on a systematic kinetic study of the oxidation of 5-oxo acids by N-Bromosuccinimide.

2. Methodology

Different methods used to study chemical kinetics. The methods are used for kinetic investigation depends on the half time period or completion time period. The extreme fast reactions are studied using molecular beam flow, stopped flow etc. techniques while other reactions can be monitored by pH-metry, conductometry and colorimetry titrations etc. The different methods used are summarized in the table 1.

Table 1: Various methods used for kinetic study

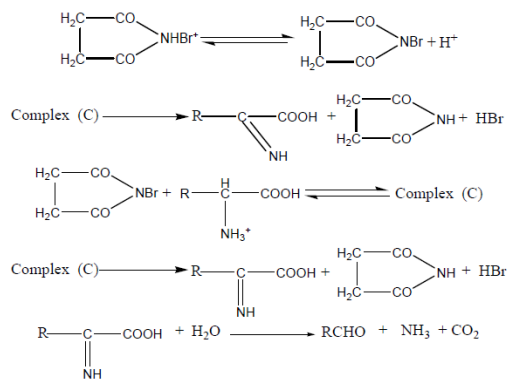
Method and time scale	Description
Conventional ≥ 10 s	1 Mix the reactants together in a batch reactor. 2 Measure concentration Vs time.
Stopped flow $\geq 10^{-1}$ s	1. Set of continuously flow system where reactants are fed into the reactor and flow out again so quickly that there is negligible reaction. 2. Stop the flow so that reactant reacts. 3. Measure the conversion Vs time.
Pressure Jump and Temperature Jump $\geq 10^{-6}$ s	Nobel prize was given for this technique to Eigen. 1. Mix the reactants at such a low temperature that the reaction rate is negligible. 2. Use CO ₂ lasers to suddenly heat the reaction. 3. Measure concentration Vs time. 4. Measure the reactant concentration Vs time.
10^{-9} - 10^{-10} s	Nobel prize was given for this technique to Porter. 1. Put the reactants into a vessel under conditions where reaction is negligible. 2. Pulse a laser flash lamp to start reaction. 3. Measure the reactant concentration Vs time.
NMR 10^{-2} - 10^{-9} s	1. Initiate a change with magnetic pulse. 2. Measure the decay of spins by NMR.
Molecular Beam 10^{-9} - 10^{-13} s	Nobel prize was given for this technique to Hersch Feld. 1. Direct Beams of reactants towards each other in a vacuum system. 2. Measure the steady state reaction rate.
Femto spectroscopy 10^{-15} s	Nobel prize was given for this technique to Ahmed Zewel. 1. Life time reaction can be studied.

3. Results and Discussion

The species which oxidizes other species give up oxygen or electronegative atom which accept hydrogen or any other electropositive element which gain electron are called oxidizing agents. There are large numbers of compounds which can be used as oxidizing agents in organic chemistry. Classification of these compounds is complicated and difficult. Although the oxidation of medicinal drugs, in the present study is carried out by potassium permanganate, it is necessary to have a look into the different oxidizing agents available.

The N haloamine has diverse nature of its ability to furnish halonium cations, hypo species, an N anion which acts as both bases and nucleophile. These compounds contain positive halogen and are mild oxidants [5]. The various compounds of which oxidation kinetics was investigated in the literature include. N-Chloronicotinamide which is reported to oxidized cyclohexanol [6]. N-Bromosuccinamide is a common name of 1-Bromo-2,5-pyrrolidinedione, with molar mass 177.98.

N- Bromosuccinimide oxidation [7] of L-arginine in aqueous acidic medium is first order in [NBS], fractional order in [L-arginine] and of inverse fractional order in [H⁺]. The suggested mechanism was



N-Bromosuccinamide is successfully used to study kinetics and mechanism of oxidation of aliphatic Ketone^[8], 5-aminopyrazoles^[9], 1-2 diaols^[10]. Polyhydric alcohols^[11], Lysozyme^[12], norephedrine^[13], D-arabinose^[13], D- xylose and D- galactose^[14], secondary alcohols^[15]. Amines^[16], acid red due^[17], diamine^[18], silicone^[19], vanillin^[20], caffeine^[21] and thiols^[22] are oxidized by N- chlorobenzene sulphonamide.

4. Conclusion

The kinetics of oxidation of gabapentin (GBP) by N-bromosuccinimide (NBS) in an alkaline medium has been studied spectrophotometrically. In acid solutions, the oxidation reaction of gabapentin by N-bromosuccinimide exhibited classical kinetics, where the reaction rate was first order dependence on [NBS], fractional order on both [GBP] and [H⁺] and increased with temperatures over (303-321oK) range. In an alkaline medium (the presented work), the reaction exhibited a unique kinetics, where the reaction rate was first order dependence on [GBP], fractional order on[H⁺] and zero order for a limited period of time dependence on [NBS]. It is noteworthy that the reaction rate decreased with increasing temperatures over (25-40°C) range. This may be explained in the light of a multistep reaction mechanism in which, the slowest step is highly exothermic. An inner-sphere mechanism for the oxidation of gabapentin by N-bromosuccinimide in an alkaline aqueous solution supported by free radical intervention was proposed.

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