



## Kinetic Screening and Mechanistic Investigations of Oxygenation of 5-Oxo Acids by N-Bromosuccinimide in Acid Medium

Sunitha Manjari Padma

Department of Chemistry, University College of Science, Saifabad, Osmania University,  
Hyderabad-500 004, **INDIA**

Email: [psmanjari76@gmail.com](mailto:psmanjari76@gmail.com)

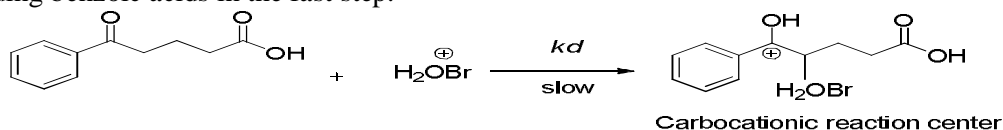
Accepted on 1<sup>st</sup> September 2017, Published online on 27<sup>th</sup> September 2017

### ABSTRACT

The kinetics and mechanistic investigation of oxidation of substituted 5-oxo-5-phenylpentanoic acids (commonly known as 5-oxo acids) by N-bromosuccinimide (NBS) has been studied in aqueous acetic acid medium. The reaction follows first order dependence in [NBS], [H<sub>2</sub>SO<sub>4</sub>] and [5-oxoacid]. Decrease in the dielectric constant of the solvent enhanced the rate of reaction. Variation of ionic strength does not influence the rate and reaction failed to induce polymerization of added acrylonitrile. Oxygenation rate is accelerated by the presence of electron-donating substituents on the phenyl ring of 5-oxo acids and is retarded by the electron-withdrawing substituents. The linear free energy relationship is characterized by the linearity in Hammett plots of log *k* against  $\sigma$ . The reaction constant is negative and decreases with increase in temperature. Isokinetic relationship is discussed from the intersection lines of Arrhenius and Hammett plots. The mechanism proposed involves the attack of protonated species of N-bromosuccinimide (H<sub>2</sub>O<sup>+</sup>Br) on the enol form of 5-oxo acids forming a carbocationic reaction center, which by carbon-carbon bond cleavage yield the corresponding benzoic acids in the fast step. The reaction is an example of neighboring group participation in intramolecular catalysis and is potentially useful for the regioselective synthesis of substituted benzoic acids in quantitative yields.

### GRAPHICAL ABSTRACT

The kinetics and mechanistic investigation of oxidation of substituted 5-oxo-5-phenylpentanoic acids (commonly known as 5-oxo acids) by N-bromosuccinimide (NBS) has been studied in aqueous acetic acid medium. The reaction follows first order dependence in [NBS], [H<sub>2</sub>SO<sub>4</sub>] and [5-oxoacid]. The linear free energy relationship is characterized by the linearity in Hammett plot of log *k* against  $\sigma$ . The mechanism proposed involves the attack of protonated species of N-bromosuccinimide (H<sub>2</sub>O<sup>+</sup>Br) on the enol form of 5-oxo acids forming a carbocationic reaction center, which by carbon-carbon bond cleavage yield the corresponding benzoic acids in the fast step.



**Keywords:** 5-Oxoacids, N-Bromosuccinimide, Kinetics, Isokinetic Relationship.