



Research Article

## Kinetics of Enolisation of Acetophenone and p-Bromoacetophenone: Comparative Studies

Swati Malhotra<sup>1</sup>, Dipika Jaspal<sup>2\*</sup>

<sup>1</sup> Department of Chemistry, SLP Science College Gwalior, Madhya Pradesh, India

<sup>2</sup> Department of Applied Science, Symbiosis Institute of Technology, Symbiosis International University, Lavale, Pune, Maharashtra, India

Received: 23rd March 2013; Revised: 21st June 2013; Accepted: 30th June 2013

### Abstract

Biomolecules (Amino Acids) have been used as catalysts for the study of kinetics involved in enolisation of acetophenone and p-bromoacetophenone, and comparative study has been carried out. The process of enolisation has been studied by halogenation reactions using iodine. The stoichiometry was determined in each case and the kinetic reactions have been carried out to study the effect of catalyst and temperature. The enolisation process has been investigated as a bimolecular reaction. The rate of enolisation was of the order p-Bromoacetophenone > Acetophenone depending on the type of substituent. The process studies follow Arrhenius equation. Values for various thermodynamic parameters like entropy ( $\Delta S^\ddagger$ ) and enthalpy ( $\Delta H^\ddagger$ ) were found to be -2.126 e.u. & -10.88 e.u. and 19.06 kcal.mol<sup>-1</sup> & 19.01 kcal.mol<sup>-1</sup> for acetophenone and p-bromoacetophenone, respectively. © 2013 BCREC UNDIP. All rights reserved

**Keywords:** Amino Acids; Acetophenone; Enolisation; p-Bromoacetophenone; Catalysis

**How to Cite:** Malhotra, S., Jaspal, D. (2013). Kinetics of Enolisation of Acetophenone and p-Bromoacetophenone: Comparative Studies. *Bulletin of Chemical Reaction Engineering & Catalysis*, 8(2): 105-109. (doi:10.9767/bcrec.8.2.4653.105-109)

**Permalink/DOI:** <http://dx.doi.org/10.9767/bcrec.8.2.4653.105-109>

### 1. Introduction

The phenomenon of enolisation is of utmost significance in the chemistry of aldehydes and ketones. The rate of enolisation is significantly affected by various factors like temperature, concentration and presence of catalyst. There has been no substantial study made on the enolisation reactions of acetophenone and p-bromoacetophenone till date as per the literature survey. Therefore this being the motivation, kinetics of enolisation reactions has been investigated for acetophenone and p-

bromoacetophenone under various conditions like temperature, concentration in the presence of catalysts.

Enolisation reactions can be studied by deuteration, recemization and halogenations [1-5]. Halogenation reaction, primarily iodination has been considered for the study of enolisation kinetics in the present research.

Kinetics of the process has been studied for the effect of the use of amino acids as catalyst. Amino acids and biomolecules viz. glycine and  $\beta$ -alanine which were obtained by the degradation of the proteins were tested as catalysts in the study of enolisation [6]. Glycine and  $\beta$ -alanine catalyzing the enolisation reaction contain two reactive groups, amino and a carboxyl group. These amino acids exist in

\* Corresponding Author.

E-mail: [sheriedipika\\_k@yahoo.co.in](mailto:sheriedipika_k@yahoo.co.in) (J. Dipika),  
Tel: +91-020-39116454, Fax: +91-020-39116260

the form of an internal salt known as Zwitter ion which is a dipolar ion.

The rate of the reaction has been studied and different thermodynamic parameters have been calculated. The present research will be helpful in understanding the chemistry behind the enolisation process and studying to what extent the different factors affect the rate of enolisation [7-15].

## 2. Materials and Methods

Kinetic runs were carried out in a thermostat (England Make) of 10 liter capacity fitted with an automated stirrer. Corning burette of grade 'A' was used for performing the titrations. Throughout the investigations glassware of borosil was used. Acetophenone was procured from B.D.H England and p-Bromoacetophenone from Kochlight laboratories Ltd. Calnbrook bucks, England and both were of A.R. grade.

Stock solutions of 0.1 M concentration were prepared by dissolving weighed amount of the ketones in 100% acetic acid, as these were insoluble in alcohol. 1 M stock solution each of different amino acids was made in bidistilled water and was used within two days, after which fresh solutions were again made.

### 2.1. Kinetic Measurement of Enolisation

Long neck stoppered flasks were taken one of these containing 0.1 M ketone and the other with the reactants i.e. acetic acid, water and iodine. The flasks were thermostated at the desired temperature for about 30 min. 5 ml of the ketone was added to the flask containing the reactants and shaken thoroughly. An aliquot was immediately withdrawn and quenched in ice cold water in a 100 ml conical flask after which the amount of iodine was estimated by titration with  $3 \times 10^{-3}$  M Hypo solution using starch as an indicator. This indicated the concentration of iodine at zero time. The process was continued by withdrawing 5mL aliquots at regular time intervals and determining the iodine used.

The rate constant in the above case can be represented as:

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad (1)$$

Here,  $k_1$  the specific reaction rate,  $a$ , is the initial concentration of iodine at zero time and  $x$  is the amount of iodine consumed in time  $t$ .

### 2.2. Variation of Amino Acids

A variation in the concentration of the amino acids was made in the range of  $10.0 \times 10^2$  to  $22.0 \times 10^2$  M and the concentration of the other reagents were kept constant. Studies were carried out at intervals of 30 min. This variation was done in the usual way taking the stock solutions and the rate constants were noted.

### 2.3. Effect of temperature

The effect of temperature differs in case of unimolecular (high activation energy) and bimolecular reactions (Low activation energy). In order to test the applicability of Arrhenius equation (Eqn. 2) iodometric measurements were carried out at different temperatures ranging from 318 K to 333 K maintaining the concentration of the substrate and the amino acids constant.

$$k_1 = A \exp \left( \frac{-E_a}{RT} \right) \quad (2)$$

The rate constant ( $k_1$ ) was first calculated and was plotted against the reciprocal of the absolute temperature (Figure 1). The slopes and intercepts of this graph provided the Arrhenius parameters. Various other thermodynamic parameters such as energy of activation ( $E_a$ ), entropy of activation ( $\Delta S^\ddagger$ ), frequency factor  $\log PZ$  ( $A$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy ( $\Delta F^\ddagger$ ) were calculated using the below mentioned mathematical expressions:

$$E_a = 2.303 \times \text{slope} \times 1.99 \times 10^{-5} \quad (3)$$

$$\log PZ = \log A = \text{intercept} T^{-1} \quad (4)$$

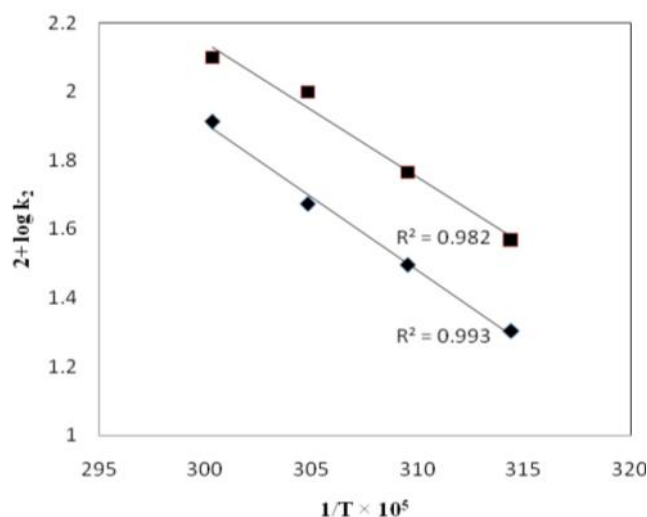


Figure 1. Arrhenius plots for Acetophenone and p-Bromo acetophenone

$$PZ = \frac{KT}{h} e^{\frac{\Delta S^\ddagger}{R}} \quad (5)$$

$$A = 10^{13} \cdot e^{\frac{\Delta S^\ddagger}{R}} \quad (6)$$

$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (7)$$

In the above expressions K is the Boltzmann constant, h is the Plank's constant, T is the absolute temperature and R is the universal gas constant.

Equation (6) clearly indicates that positive or negative value of  $\Delta S^\ddagger$  will depend upon whether A is greater or smaller than  $10^{13}$ . A positive value of  $\Delta S^\ddagger$  i.e.  $A > 10^{13}$  will corresponds to a more probable complex formation and the reaction is faster than the normal one.

The specific rate constants were calculated as per the equation given below:

$$k_2 = \frac{k_1}{[\text{ketone}] \times 60} \quad (8)$$

### 3. Results and Discussion

#### 3.1. Variation of Catalyst

Amino acids like  $\beta$ -alanin and glycine were tested as catalysts in the enolisation process for the two ketones as these are expected to show different catalytic activity. Amino acids form two equilibria involving three kind of species. At about pH 6.0, dipolar ion (Zwitter ion) species exists, which is converted to more protonated acid form with positive charge on nitrogen. At lower pH range however it is converted into more anionic species with a negative charge on oxygen. Since the rates of enolisation of the ketones are proportional to the concentration of amino acids hence the rates of enolisation are expected to be governed by the

concentration of Zwitter ion species.

The velocity constants in this case to were found to increase with the increase in the concentration of the amino acids (Table 1). As in the above case p-bromoacetophenone again shows higher rate constant values [16, 17]. The two amino acids show different catalytic effects by virtue of their different dipole moments ( $\beta$ -alanin 19.4D > glycine 11.6-15.7 D). The greater the dipole moment of the amino acid more is the separation of charge in the molecule and greater is the rate of enolisation. The obtained value in Table 2 were well in agreement however among the two amino acids the order of rate constants for  $\beta$ -alanin were of the order p- Bromoacetophenone > Acetophenone whereas for glycine Acetophenone > p-Bromoacetophenone.

#### 3.2. Variation of Temperature

Plots of  $\log k_2$  versus  $1/T$  give straight lines ( $R^2 = 0.993$  and  $0.982$  for Acetophenone and p-Bromoacetophenone, respectively) confirming the applicability of Arrhenius equation [16, 17]. The slopes of these graphs were utilized for the calculation of Arrhenius parameters (Table 2 and 3). The data obtained from these studies have been portrayed in Tables 2 and 3. The magnitude of the parameters obtained, are indicative of the bimolecular nature of the enolisation reactions.

The rates are found in the order p-Bromoacetophenone > acetophenone, thereby confirming that the presence of electron attracting groups facilitates the formation of enol thereby enhancing the rate. The findings are in accordance with the studies made by Hammett [18], according to whom the rate of any of the substituted compounds is related to the value for the unsubstituted compounds in terms of two parameters  $\sigma$  and  $\rho$ . In the case of the rate constant the relationship is:

**Table 1.** Comparison of the rates of enolisation in the two ketones (Temp: 50 °C) [Ketone] = 0.1 M, [Iodine] = 0.006 M, [AcOH] = 20 % (v/v)

Exp. No.	Amino Acid ( $M \times 10^2$ )	4 + log $k_1$			
		Acetophenone		p-Bromoacetophenone	
		$\beta$ -alanin	glycine	$\beta$ -alanin	glycine
1	10.0	3.5211	3.3978	3.7040	3.400
2	14.0	3.6504	3.5146	3.7315	3.421
3	18.0	3.7702	3.5914	3.854	3.4757
4	20.0	3.8414	3.6162	3.889	3.4910
5	22.0	3.8652	3.6468	3.930	3.5310

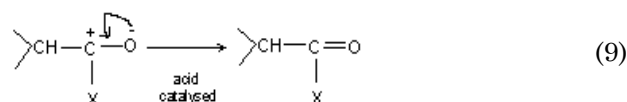
**Table 2.** Thermodynamic Parameters (Temp. 318 K) [Ketone] = 0. 1M, [Iodine] = 0.006 M, [β-alanin] = 0.1 M, AcOH = 20% (v/v)

Ketone	ΔEa (kcal mol <sup>-1</sup> )	Pz (l mol <sup>-1</sup> min <sup>-1</sup> )	ΔS <sup>‡</sup> (e.u.)	ΔH <sup>‡</sup> (K. cal mol <sup>-1</sup> )	ΔF <sup>‡</sup> (K. cal mol <sup>-1</sup> )
Acetophenone	19.05	2.42 × 10 <sup>12</sup>	-2.126	19.06	22.98
p-Bromoacetophenone	19.06	4.4 × 10 <sup>14</sup>	-10.88	19.01	22.53

**Table 3.** Effect of Temperature (K). [Ketone] = 0.1M, [Iodine] = 0.006M, [β-alanine] = 0.1M, [AcOH]=20%

Temperature (K)	318	323	328	333
<b>Acetophenone</b>				
1/T × 10 <sup>5</sup>	314.4	309.5	304.8	300.3
k <sub>2</sub> (k <sub>1</sub> /subs.conc.) l. mol <sup>-1</sup> min <sup>-1</sup>	0.20	0.31	0.47	0.81
2 + log k <sub>2</sub>	1.30	1.49	1.67	1.91
5 + log k <sub>2</sub> /T	1.79	1.98	2.12	2.38
<b>p-Bromoactophenone</b>				
1/T × 10 <sup>5</sup>	314.4	309.5	304.8	300.3
k <sub>2</sub> (k <sub>1</sub> /subs. conc.) l. mol <sup>-1</sup> min <sup>-1</sup>	0.36	0.58	0.95	1.14
2 + log k <sub>2</sub>	1.56	1.76	1.99	2.10
5 + log k <sub>2</sub> /T	2.05	2.25	2.46	2.52

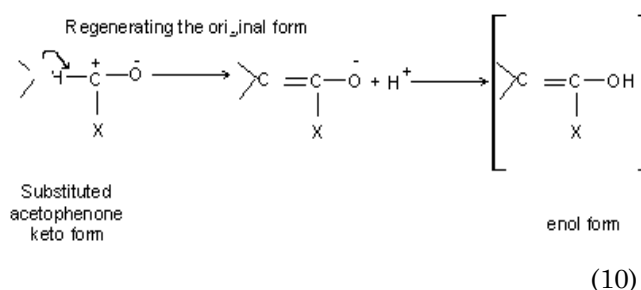
$$\log k = \log k_0 + \sigma\rho \quad (9)$$



where,  $k_0$  is the rate constant of the parent compound. The parameter  $\sigma$  depends only on the substituent whereas  $\rho$  is the reaction constant. Substituent with positive  $\sigma$  values, are strong electron attractors and with negative values are weak electron attractors. Reactions with positive  $\rho$  values take place at a faster rate due to electron withdrawal from the benzene ring, whereas those with negative values are retarded by electron withdrawal.

The results of the rates obtained in the present experimentation with positive and negative substituents constant (CH<sub>3</sub> (-0.07) & Br (0.39)) were in accordance with Hemmett. This further confirms that the electron attracting groups increase the rate whereas the electron repelling groups show an adverse affect on the rate.

The mechanism has been explained by chemical Equations (9) & (10) as follow:



A significant work was done by Watson et al. [19] has suggested that in a proper collision, at appropriate temperature with acid catalyst, energy is communicated to the groups and semipolar form becomes the main participant in the resonance state. This is then followed by an immediate transformation either regenerating the original form as per Equation (9) or leading to the production of the enol form according to Equation (10).

At this point the rate of the prototropic change depends upon the speeds of reaction of ketone and the catalyst and also the proportion of the energised form present which undergoes transformation as shown in Equation (10).

#### 4. Conclusions

It is concluded that the rate of enolisation in case of both the ketones is dependent upon the concentration of amino acids and temperature. Substituted acetophenone, i.e. p-bromoaceto-phenone, shows greater reaction velocities in comparison to acetophenone due to the presence of electron withdrawing bromo group. The enolisation is found to be bimolecular reaction in nature. The  $\beta$ -alanin shows greater reaction rates in comparison to glycine for both the ketones.

#### Acknowledgments

One of the authors (SM) is thankful to CSIR for the fellowship provided for the research.

#### References

- [1] Fontana, A., and More O'Ferrall, R.A. (1994). Equilibrium Constants for Ionisation and Enolisation of 2-Phenylacetyl furan. *J. Chem. Soc. Perkin Trans.*, 212: 2453-2459.
- [2] Khirwar, S.S. (2010). Kinetics of the Enolisation of p-Ethoxyacetophenone Catalysed by Amino Acids. *Oriental J. Chem.* 26: 1037-1042.
- [3] Maria, P. D., Fontana, A., Siani, G., Spinelli, D. (1998). Kinetics of the Enolisation Reactions of 3-acetyl-2,5-dimethylfuran and of 2-Acetyl-selenophene. *Eur. J. Org. Chem.* 9: 1867-1872.
- [4] Ahmed, M.K.S., Bharatam, P.V. (2005). Importance of sulfoxidation in rapid racemisation of glitazones. *Indian J. Chem.* 44: 600-606.
- [5] Ariza, X., Asins, G., Garcia, J., Hegardt, F.G., Makowski, K., Serra, D., Velasco, J. (2010). Preparation of  $\alpha$ -labeled aldehydes by base-catalyzed exchange reactions. *J. Labell. J. Comp. Radiopharm.* 53: 556-558.
- [6] Craig, W. M., Broderick, G. A. (1984). Amino Acids Released During Protein Degradation By Rumen Microbes. *J. Anim. Sci.* 58: 436-443.
- [7] Dobhal, B., Farooqui, M., Ubale, M. (2010). Kinetics of Permagnetic oxidation of 4-hydroxy Benzaldehyde in acidic media. *Int. J. Chem. Tech. Res.* 2: 443-446.
- [8] Singh, B., Pandey, L., Sharma, J., Pandey, S.M. (1982). Mechanism of oxidation of some aliphatic ketones by N-bromosuccinimide in acidic media. *Tetrahedron* 38: 169-172.
- [9] Tandon, P.K., Kumar, S., Srivastava, M., Khanam, S. Z., Singh, S. B. (2007). Oxidation of hydrates of cyclic ketones by alkaline hexacyanoferrate(III). *J. Mol. Cat. A: Chem.* 261: 282-287.
- [10] Tandon, P. K., Sehgal, S., Singh, A. K., Kumar, S.M. (2006). Oxidation of cyclic ketones by cerium(IV) in presence of iridium(III) chloride. *J. Mol. Cat A: Chem.* 258: 320-326.
- [11] Raillard, C., Hequet, V., Cloirec, P., Le Legrand, J. (2004). Kinetic study of ketones photocatalytic oxidation I gas phase using TiO<sub>2</sub> containing paper: effect of water vapor. *J. Photochem. Photobiol. A: Chem.* 163: 425-431.
- [12] Zacuto, M. J., Cai, D. (2005). Iodine-mediated Z-selective oxidation of ketones to  $\alpha,\beta$ -unsaturated esters: synthesis and mechanistic studies. *Tetrahedron Letters* 46: 8289-8292.
- [13] Mahadevappa, D.S., Mohan, K., Ananda, S. (1986). Electrolytic partial fluorination of organic compounds. Part 48: Anodic fluorination of 2-cyano-1-methylpyrrole. *Tetrahedron* 42: 4857-4860.
- [14] Escobar, G.P., Beroy, A.Q., Pina Iritia, M.P., Huerta, H. (2004). Kinetic study of the combustion of methyl-ethyl ketone over  $\alpha$ -hematite catalyst. *Chem. Eng. J.* 102: 107-117.
- [15] Agarwal, A., Sharma, G., Khandelwal, C.L., Sharma, P.D. (2002). Kinetics and Mechanism of Oxidation of Mannitol by Sulphato-cerium(IV) Species in Aqueous Acid Medium. *Inorg. React. Mech.* 4: 233-239.
- [16] Malhotra, S., Jaspal, D. (2011). Study of Effect of Catalyst and Solvent on the Enolisation Process of p-Bromoacetophenone. *Bull. Catal. Soc. India.* 10: 1-6.
- [17] Malhotra, S., Jaspal, D. (2012). Kinetics of Amino Acid Catalyzed Enolisation of Acetophenone. *J. Chem. Pharm. Res.* 4: 239-245.
- [18] Hansch, C., Leo A., Taft, R. W. (1991). A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev.* 91: 165-195.
- [19] Watson, H.B., Nathan, W.S., Laurie, L. L. (1935). The Acidities of Ketones and the Mechanism of Prototropic Change. *J. Chem. Phys.* 3: 170-174.