



# Effects of ionic strength on the reaction rate between aromatic aldehydes and tertiary butyl hypochlorite

Venu Sangal

Dept. of Chemistry, School of Vocational studies and Applied Sciences, Gautam Buddha University, G. Noida, UP, India  
venu\_sangal@yahoo.com

Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

Received 6<sup>th</sup> June 2020, revised 20<sup>th</sup> August 2020, accepted 23<sup>rd</sup> September 2020

## Abstract

*The effect of adding different concentrations of sodium perchlorate on the rate of reaction between aromatic aldehydes viz. p-methoxybenzaldehyde, p-methylbenzaldehyde, benzaldehyde, p-chlorobenzaldehyde and, p-nitrobenzaldehyde and t-BuOCl was studied at 35°C. The results show that the ionic strength has no significant effect on the reaction rate. This indicates that the nature of reactions are not ionic and reactions take place between molecules.*

**Keywords:** Kinetic studies, ionic strength, aromatic aldehydes, tertiary butyl hypochlorite, bronsted-bjerrum equation.

## Introduction

Mechanism of chemical reactions is a subject of considerable importance because not only does it require the consideration of the properties of both inorganic and organic compounds, but it does have vast implications in understanding the nature of life. Hence the study of reaction mechanism has attracted the attention of chemists.

**Importance of Kinetic Studies of Chemical Reactions:** To understand how a chemical reaction occurs, it is essential to follow the kinetics of the reaction. Although the kinetic studies provide the most powerful tool for investigation of the mysteries of a reaction, it is not always possible to gather complete information about the reaction by kinetic studies alone. However, the chemical kinetics still remain the most powerful weapon in the armory of a chemist in attacking the problem of a reaction pathway. The kinetics of a reaction allows a deeper insight into the probable modes of the chemical change.

The chemical changes of organic compounds in general are not simple one-step conversions; these normally occur in number of steps that take place either simultaneously or follow one after the other. Thus, the study of the chemical kinetics becomes all the more important to the organic chemist, because the course and products of a very large number of organic reactions are controlled by the relative rates of several competing reactions, and it is only by understanding the dependence of the various rates on the reaction variables viz. concentration, temperature, solvents etc., that one can predict the conditions required for favoring the desired product. Further, knowledge of the mechanism by which the reactants are converted into products has proved of value in several ways and for obtaining this information, a study of the kinetics of the reaction, coupled with other studies, provides one of the most satisfactory ways one of the most satisfactory ways is to study the kinetics of reaction

along with some other studies. Even in those cases where kinetic studies alone are incapable of delivering the desired information; enough kinetic data can be gathered to show that one mechanism is more probable than the other.

In any case, the core of understanding the intricacies of a reaction is the evaluation of the reaction rate. Thus, the utility of kinetic studies cannot be over-emphasized.

**Importance of solvent effects in kinetics of chemical reactions:** A large number of chemical transformations are brought about in solutions. The problem of interpretation and analysis of rate of such reactions, from the molecular viewpoint, is a rather complicated one because every molecule in a solution at any point of time comes in close contact with about 4 to 12 nearby species. Thus, in any chemical reaction, a very large number of neighbouring molecules arbitrarily and randomly intrude upon the intimate mechanical motions of the atoms and the electrons of every molecule. Therefore, experimental determination of the rate law for a reaction in solution poses difficulties in interpretation as different mechanisms may have the same rate law. The serious drawback in the interpretation of experimental rate law in terms of mechanism is the possible involvement of the solvent molecules in the reaction process. Since the effective concentration of the solvent does not vary appreciably, its effect on rate and hence its participation in various stages of reaction remains obscure in most cases. Though, significant advances<sup>1,2,3,4</sup> have been made in terms of the correlation of the rates of various types of reactions with the dielectric constants of the media, yet the exact role of the solvent molecules in mechanism, especially on electron distribution and reactivity of reactant species is not fully understood. Importance of solvent effects may be realized from the fact that although a very large number of reactions were studied in solution, only a few could be carried out in gaseous state.

**Connection between chemical reactivity of a molecule and its structure:**

Another aspect of interest in kinetic studies is the relation between the chemical reactivity of a molecule and its structure. For many years the chemists have been challenged by the problem of evaluating the influence of substituents on the course and the rate of reaction. The main difficulty in the determination of the electronic substituent effect arises from the fact that a substituent, if close to reaction site, may influence the reaction by pure steric processes and thus overshadow the electronic effects; and if, for removing steric factors, the substituent is placed far away, the electronic effects will be very much reduced. The first major breakthrough in this area was made by Hammett<sup>5</sup>, who developed a simple relationship for analysing the electronic-substitution effects on rates of the aromatic compounds, having substituents in the benzene ring at meta or at para positions. Following the idea and reasoning advanced by Hammett, Taft<sup>6,7</sup> established another relationship between the reactivity of aliphatic compounds and the substituents present in the reactants. These correlations are based on the changes in free energies of the compounds differing only in the substituents present in the molecule and have been developed on the basis of empirical constants. These correlations are linear for one variable at least and are usually referred to as 'linear free energy relationships'<sup>8</sup>. An alternative phrase used for these is 'extra-thermodynamic relationships' because they exhibit thermodynamic relationships between quantities which do not obey the laws of thermodynamics. Obviously, such relationships can be applied, as in thermodynamics, even without full knowledge of the mechanism of reaction.

The linear free energy relationships i.e. extra-thermodynamic relationships are helpful in summarizing and understanding the effect of the structure of molecule on chemical reactivity.

**Relation between Ionic Strength and Reaction Rate:** The salt effect occupies a key position in the theory of reaction rates in solution. Since ions exert considerable electrostatic forces on each other on distances much greater than their collision diameters, they cannot be treated as ideal solute species. The active concentration of an ion is strictly given by its activity 'a' which is the product of its actual concentration 'C' and an activity coefficient 'f' which is less than unity except in infinitely dilute solutions, that is,

$$a = C \cdot f \leq C$$

As per the theory of the transition state, the reaction rate  
 $A + B \rightleftharpoons AB^\ddagger \rightarrow \text{Products}$

$$\text{is } -\frac{d[A]}{dt} = \frac{kT}{h} [AB^\ddagger]$$

$$= k [A] [B]$$

k, the rate constant of the experiment, is measured in terms of concentrations [A] and [B] to which it is related by

$$k = \frac{\kappa T}{h} \frac{[AB^\ddagger]}{[A][B]}$$

If A and B are ions, the equilibrium constant  $K^\ddagger$  for the formation of the activated complex  $AB^\ddagger$  is given by

$$K^\ddagger = \frac{a_{AB^\ddagger}}{a_A a_B} = \frac{[AB^\ddagger]}{[A][B]} \frac{f_{AB^\ddagger}}{f_A f_B}$$

$$\text{hence } k = \frac{\kappa T}{h} K^\ddagger \frac{f_A f_B}{f_{AB^\ddagger}} = k_0 \frac{f_A f_B}{f_{AB^\ddagger}} \quad (1)$$

$k_0$  being the rate constant at infinite dilution when  $f_A = f_B = f_{AB^\ddagger} = 1$ . Thus any added substance which changes the transition state and activity coefficients of the reactants will change the measured rate of reaction.

In dilute solutions the activity coefficient 'f' of an ion of charge 'Z' is related to the ionic strength 'μ' of the solution by the Debye-Huckel expression:

$$-\log f = 0.5 Z^2 \sqrt{\mu}$$

$$\text{so that } \log \frac{f_A f_B}{f_{AB^\ddagger}} = -0.5 \sqrt{\mu} (Z_A^2 + Z_B^2 - Z_{AB^\ddagger}^2) \quad (2)$$

As the charge of the activated complex  $Z_{AB^\ddagger}$  is equal to the algebraic sum of the ionic  $Z_A$  and  $Z_B$  that is,  $Z_{AB^\ddagger} = Z_A + Z_B$ , so the equation (2) becomes

$$\log \frac{f_A f_B}{f_{AB^\ddagger}} = Z_A Z_B \sqrt{\mu}$$

which may be substituted in the logarithmic form of equation (1)

$$\log k = \log k_0 + \log \frac{f_A f_B}{f_{AB^\ddagger}} \text{ to give } \log k = \log k_0 + Z_A Z_B \sqrt{\mu} \quad (3)$$

The expression (3) is known as the Bronsted-Bjerrum equation<sup>9</sup>.

Now, if  $\log (k/k_0)$  is plotted against  $\sqrt{\mu}$  (ionic strength) for a number of reaction ions; in each case we find that slope equals the product of the charges of the reacting ions  $Z_A Z_B$ . The slope of -1 indicates that the reactants are ions. According to Lewis and Randall<sup>10</sup>, the ionic strength is a measure of the intensity of electric field, due to the ions in solution. The ionic strength  $\sqrt{\mu}$  of a solution is defined by them as half the sum of the individual ionic concentrations each multiplied by the square of the ionic charge, that is,

$$\sqrt{\mu} = \frac{1}{2} \sum C_i Z_i^2$$

Where:  $C_i$  is the actual concentration of each ion and  $Z_i$  its valency.

According Bronsted-Bjerrum<sup>9</sup> equation (3) the addition of any salt will have a marked effect on the rate of a reaction between ions in solution even though it exerts no chemical effect. If the reacting ions have the same charge then  $Z_A Z_B$  is positive and the

addition of a salt will increase the reaction rate; but if ions are of opposite charge then  $Z_A Z_B$  is negative and the rate is reduced by the increase in ionic strength due to the added salt. If one of the reactant is neutral then  $Z_A Z_B$  is zero and the rate constant is expected to be independent of ionic strength<sup>11,12</sup>.

Bronsted<sup>13,14</sup> suggested that for ionic reactions in solutions, it is essential to keep the ionic strength constant throughout for a comparative study. In such cases the primary and secondary salt effects influence the velocity of the reaction when reactions are performed in solutions of varying ionic strength. The primary salt effect is concerned with the effects of salts on the activity coefficients of the reactants and the activated complex formed as an intermediate in the reaction while the secondary salt effect is concerned with the influence of ionic strength of the medium on the concentration of catalytically active ions. For example, in a solution containing a buffer (of formic acid and sodium formate) if we change buffer concentration (ratio remains constant) and also ionic strength, then if  $k$  changes, there is a secondary salt effect.

## Materials and methods

One of the prerequisites of the kinetic studies is the utmost purity of reagents and solvents, especially the redox reactions are highly sensitive to traces of impurity. Hence great care has been taken to secure and maintain the purity of the compounds and solvents used.

**Reagents:** Chlorine was prepared by treating potassium permanganate (B.D.H. AnalaR) with concentrated hydrochloric acid (B.D.H. AnalaR) in a flask and passing the gas thus produced through the bubblers containing  $KMnO_4$  solution.

**Preparation of t-BuOCl:** t-BuOCl was prepared by passing  $Cl_2$  into cold aqueous sodium hydroxide and t-butyl alcohol (B.D.H.) as described by Chattaway Backeberg<sup>15</sup>. Teeter and Bell<sup>16</sup> also described the same method.



The hypochlorite was purified by distillation in an all glass apparatus, b.p.  $80^\circ C$  and stored in coloured bottles at about  $0^\circ C$ . Caution was exercised during preparation and separation to

prevent exposure to strong light. It is a stable yellow liquid, having viscosity at  $25.2^\circ C = 0.543$  centipoise<sup>17</sup> with a characteristic irritating odour. Its normality was calculated by thiosulphate titration of iodine liberated from potassium iodide in the presence of acetic acid.

All aldehydes used were B.D.H. (AnalaR) or Merck (C.P.) grade or of comparable purity and were recrystallised or redistilled before use.

Anala R grade perchloric acid (Merck) solutions were standardized against carbon dioxide free standard sodium hydroxide solution.

Throughout alkaline permanganate redistilled water was used. All other chemicals were either B.D.H. (AnalaR) or Merck (C.P.) grade or of comparable purity.

**Kinetic Procedure:** We controlled the thermostat within  $\pm 0.1^\circ C$ . Sodium perchlorate was added to the reaction mixture to bring the ionic strength of 0.2. Before mixing, t-BuOCl solution was brought to the room temperature and then thermostated for only 3 to 5 minutes and other solutions for more than half hour. At the end of reaction unreacted t-BuOCl was estimated in 20 ml. aliquot portions of the reaction mixture at regular intervals. The aliquots were poured into ice cold distilled water containing potassium iodide and then 2ml. of glacial acetic acid was added. The liberated iodine was titrated against standard sodium thiosulphate solution using freshly prepared starch as indicator<sup>18</sup>. To avoid photochemical complications, black coloured bottles were used. Prior to each experiment, the bottles were cleaned with strong chromic acid, washed, steamed and then dried in an oven. All the studies have been performed in 50% acetic acid.

## Results and discussion

**Observations:** In this paper we have studied the influence of ionic strength on the rate of reactions of p-methoxybenzaldehyde, p-methylbenzaldehyde, benzaldehyde, p-chlorobenzaldehyde and, p-nitrobenzaldehyde with t-BuOCl by varying the amounts of sodium perchlorate. A summary of the experimental results is given in Tables-1 to 5.

**Table-1: Influence of varying ionic strength on the oxidation rate of p-methoxybenzaldehyde with t-BuOCl at  $35^\circ C$  [t-BuOCl] = 0.0004M, p-methoxybenzaldehyde] = 0.5000M, Medium: 50% AcOH.**

[ $NaClO_4$ ], M	0.20	0.25	0.30	0.35	0.40	0.50
$k_o \times 10^7$ , M sec <sup>-1</sup>	5.00	5.10	5.20	5.32	5.44	5.58

**Table-2: Influence of varying ionic strength on the oxidation rate of p-methylbenzaldehyde with t-BuOCl at  $35^\circ C$  [t-BuOCl] = 0.00065M, [p-methylbenzaldehyde] = 0.2000M, Medium: 50% AcOH.**

[ $NaClO_4$ ], M	0.20	0.25	0.30	0.35	0.40	0.50
$k_o \times 10^7$ , M sec <sup>-1</sup>	6.12	6.22	6.35	6.48	6.52	6.70

**Table-3: Influence of varying ionic strength on the oxidation rate of benzaldehyde with t-BuOCl at 35° C [t-BuOCl] = 0.00067M, [benzaldehyde] = 0.0600M, Medium: 50% AcOH.**

[NaClO <sub>4</sub> ], M	0.20	0.25	0.30	0.35	0.40	0.50
k <sub>o</sub> × 10 <sup>7</sup> , M sec <sup>-1</sup>	8.52	8.71	8.85	9.11	9.25	9.45

**Table-4: Influence of varying ionic strength on the oxidation rate of p-chlorobenzaldehyde with t-BuOCl at 35° C [t-BuOCl] = 0.0007M, [p-chlorobenzaldehyde] = 0.0400M, Medium: 50% AcOH.**

[NaClO <sub>4</sub> ], M	0.20	0.25	0.30	0.35	0.40	0.50
k <sub>o</sub> × 10 <sup>7</sup> , M sec <sup>-1</sup>	7.02	7.02	7.25	7.46	7.62	7.83

**Table-5: Influence of varying ionic strength on the oxidation rate of p-nitrobenzaldehyde with t-BuOCl at 35° C [t-BuOCl] = 0.00049M, [p-nitrobenzaldehyde] = 0.0700M, Medium: 50% AcOH.**

[NaClO <sub>4</sub> ], M	0.20	0.25	0.30	0.35	0.40	0.50
k <sub>o</sub> × 10 <sup>7</sup> , M sec <sup>-1</sup>	9.60	9.72	9.84	10.1	10.3	10.5

**Discussion:** Reaction rates of various benzaldehydes with t-BuOCl were studied with varying concentrations of sodium perchlorate at 35°C. Results are given in Tables 1 to 5, which show that ionic strength does not exert any significant influence on the reaction rate.

## Conclusion

Our observations clearly establish that there is no significant effect of the ionic strength on the rate of reaction between p-methoxybenzaldehyde, p-methylbenzaldehyde, benzaldehyde, p-chlorobenzaldehyde and, p-nitrobenzaldehyde with t-BuOCl. This fact leads to the conclusion that the nature of reactions are not ionic and the reactions take place between molecules.

## Acknowledgement

This study has been conducted under the able guidance and supervision of Dr Arun Kumar, Ex- HOD Chem. and Ex-Principal, Meerut College, Meerut. His ideas and motivation have been of immense help to me. I owe a debt of gratitude to him. I am also indebted to Dr Jaya Maitra, the Head of Chemistry Dept., GB University, Greater Noida for providing me the necessary facilities for conducting this study. Her cooperation and encouragement although are thankfully acknowledged.

## References

- Holger B. Friedrich, (1999). The Oxidation of Alcohols to Aldehydes or Ketones. *Platinum Metals Rev.* 43(3), 94-102.
- Kenneth Barbalace, (2019). Chemical Database - Tert-Butyl Hypochlorite. Environmental Chemistry. com <https://EnvironmentalChemistry.com/yogi/chemicals/cn/Tert-Butyl%AOHypochlorite.html>
- R.G. Makitra, G.G. Midyana and E.Ya. Pal'chikova (2007). Effect of the Medium on the Reaction of tert-butyl hypochlorite with hydrocarbons. *Russian Journal of General Chemistry*, 77(6), 1044-1048.
- Cristina Pastoriza, Antelo Juan and Juan Crugeiras (2013). Oxidation of Bromide with Tert Butyl Hypochlorite. *International Journal of Chemical Kinetics*, 45(10), 629-637.
- Hammet, L.P. (1937). The Effect of Structure upon the reactions of Organic Compounds. Benzene Derivatives. *J. Am. Chem. Soc.*, 59, 96-103.
- Taft, R.W., (1966). Separation of Polar, Steric and Resonance Effects in Reactivity. In: Steric Effects in Organic Chemistry (Ed. M.S. Newman). John Wiley and Sons, New York, 556-575.
- Shorter J. (1972). The Separation of Polar, Steric, and Resonance Effects by the Use of Linear Free Energy Relationships. In: Chapman N.B., Shorter J. (eds) *Advances in Linear Free Energy Relationships*. Springer, Boston, MA. [https://doi.org/10.1007/978-1-4615-8660-9\\_2](https://doi.org/10.1007/978-1-4615-8660-9_2)
- Leffer, J.E., and Grunwald, E. (1963). Rates and Equilibria of Organic Reactions. John Wiley and Sons, New York, p.171, ISBN-10: 0471523534, ISBN-13: 978-0471523536.
- B. Stevens, (1961). Chemical Kinetics. Chapman and Hall Ltd., London, p.59, ISBN- 0412207400.
- G. N. Lewis and M. Randall. (1921). The Activity Coefficient of Strong Electrolytes. *J. Am. Chem. Soc.*, 43, 1112-1154. <https://doi.org/10.1021/ja01438a014>
- A. Findley (1943). Introduction to Physical Chemistry. Longman Green & Co. p.355, ISBN 0 582 44222 2

12. Climate Policy Watcher, (2019). Ionic Strength Vs Rate Constant. <https://www.climate-policy-watcher.org/aromatic-hydrocarbons/x-1.html>
13. J. N. Bronsted, (1922). Z. Physik Chem. 102, 169-207.
14. Maria Marchena and Francisco Sanchez (2006). The Bronsted Equation: The Universal Equation?. Progress in Reaction Kinetics and Mechanism 31, 221-248, doi: 10.3184/146867806X213396
15. F.D. Chattaway and O.G. Backeberg, (1923). CCCVI. Alkyl hypochlorites. *J. Chem. Soc. Transactions*, 123, 2999-3003. <https://doi.org/10.1039/CT9232302999>
16. H.M. Teeter and E.W. Bell (1952). Tert-butyl hypochlorite. *Org. Synthesis*, 32, 20-22, DOI: 10.15227. <http://www.orgsyn.org/Result.aspx>
17. C. Walling and B.B. Jacknow. (1960). Positive Halogen Compounds. I. The Radical Chain Halogenation of Hydrocarbons by t-Butyl Hypochlorite. *J. Am. Chem. Soc.*, 82, 6108-6112 <https://pubs.acs.org/doi/10.1021/ja01508a033>
18. W.C. Bray and H.F. Miller (1924). The Standardization of Thiosulfate Solution by the Permanganate-Iodide and Dichromate-Iodide Methods. *J. Am. Chem. Soc.*, 46, 2204-2211. <https://pubs.acs.org/doi/10.1021/ja01675a010>