

Effect of Varying Acetic Acid Concentration on the Reaction Rate between Aromatic Aldehydes and Tertiary Butyl Hypochlorite

Venu Sangal *

Department of Chemistry, School of Vocational studies and Applied Sciences, Gautam Buddha University, G. Noida (UP), India

Abstract

In this paper the influence of solvent dielectric constant on the rate of oxidation of p-methoxybenzaldehyde and p-methylbenzaldehyde with t-BuOCl has been studied in various solvent mixtures of acetic acid and water. The results indicate that in the oxidation of p-methoxybenzaldehyde with t-BuOCl the rate increases with increase in the percentage of acetic acid (from 10% to 40%), but the rate decreases with further increase in acetic acid content (50-80% HOAc). In the oxidation of p-methylbenzaldehyde with t-BuOCl the rate is maximum at 50% HOAc and decreases on either side of this percentage.

Keywords:

Kinetic studies • Ionic strength • Aromatic aldehydes • Tertiary Butyl Hypochlorite, Dielectric Constant

Introduction

Many chemists have devoted considerable attention to the study of the mechanism of chemical reactions. To understand how a chemical reaction occurs, it is essential to follow the kinetics of the reaction. The kinetic studies provide a very powerful tool for investigation of the mysteries of a reaction, but complete information about the reaction cannot be gathered by kinetic studies alone. However, the chemical kinetics still remains the most powerful tool of a chemist in attacking the problem of a reaction pathway. The chemical changes of organic compounds in general are not simple one-step conversions; these normally occur in a 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 favouring the desired product. Further, knowledge of the mechanism by which the reactants are converted into products is useful in several ways and for obtaining this information a study of the kinetics of the reaction is one of the most satisfactory means. 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 determination of the rate of a reaction remains at the core of understanding the intricacies of a reaction. Thus, the utility of kinetic studies cannot be over-emphasized.

Materials and Methods

Various Oxidizing Agents

Quite a large number of Oxidizing agents are known, and these have been used in different step by step or overall oxidation reactions. Regulated oxidation has been the recognized experimental procedure for investigating the structure of any natural product from early times of the development of organic chemistry. But it is comparatively within later years that methods of oxidation have been so elaborated that one can easily select a specific reagent that can be relied upon to attack particular groups only. The commonly used oxidants for organic compounds are permanganate, dichromate, periodate, peroxydisulphate, hexacyanoferrate (III), selenium dioxide, osmium tetroxide, lead tetraacetate, ozone, hydrogen peroxide and peracids, etc. Besides some metal ions like Ce (IV), Co(III), Mn(III), Tl(III), V(V) etc. are also useful oxidizing agents. In addition to these, molecular halogens, some N-halogeno and O-halogeno compounds have been found to be effective oxidizing agents for organic substrates. Amides, imides and anilides are very weak bases because of the electron-withdrawing acyl groups attached to the nitrogen atom in these compounds. Obviously, the presence of acyl group enhances the electronegativity of nitrogen. So, when a chlorine atom is connected to this nitrogen, the chlorine acquires a positive oxidation state. Such N-chlorinated compounds are generally referred

*Address to correspondence: Venu Sangal, Department of Chemistry, School of Vocational studies and Applied Sciences, Gautam Buddha University, Noida, India, Email: Venu_sangal@yahoo.com

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to as 'positive halogen' compounds. Although alkali hypohalites are the most common halogen compounds having halogen in the +1 oxidation state, and alkyl hypohalites and N-halomides are their organic counterparts which have halogen in the +1 oxidation state. These N-halogeno have been extensively used as halogenating as well as oxidizing agents. Some of them are excellent halogenating agents, whereas others, particularly those involving the use of a polar medium and where the reaction proceeds via ionic, rather than a free radical mechanism, have proved to be strong oxidants.

Relation between chemical reactivity of a molecule and its structure

Another aspect of interest in kinetic studies is the relationship between the structure of a molecule and its chemical reactivity. A problem that has challenged the chemists for years is the determination of the influence that substituents exert on the rates and course of reaction. One of the difficulties involved in determining electronic substituent effect is that if a substituent is located close to the reaction site it may affect the reaction by purely steric processes so that the electronic effects are masked; and if placed far away, in order to avoid steric factors, the electronic effects will be severely attenuated. The first major breakthrough in this area was made by Hammett¹, 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, Taft² 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 formulated by using empirical constants. These are linear with respect to at least one variable and are usually referred to as 'linear free energy relationships'. An alternative phrase used for these is 'extra-thermodynamic relationships' involving relationships between thermodynamic quantities which do not follow the fundamental laws of thermodynamics. As in thermodynamics, these relationships can be applied without a detailed knowledge of the reaction mechanism. The linear free energy relationships are useful in summarizing and understanding the influence of molecular structure on chemical reactivity.

Importance of solvent effects in kinetics of chemical reactions

Many 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. The reason is that a particular molecule in a solution, is at any moment, in close contact with a number of nearby species which may vary from 4 to 12. Intimate mechanical motions of the atoms and the electrons belonging to a molecule (or a pair of molecules) undergoing chemical reaction are thus being constantly intruded upon in a random and arbitrary way by an imposingly large number of neighbouring molecules. 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 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 among the thousands of reactions, which have been studied in solution, only a few could be carried out in gaseous state.

Effect of varying acetic acid concentration on reaction rate

The property of solvent closely related with the polarity of solvent is the dielectric constant (D). In 1922, Scatchard gave the following equation between specific rate (k) and dielectric constant (D):

$$\log k = \log k_0 - \frac{Z_A Z_B e^2}{k D T r} \dots \dots \dots (1)$$

$$\ln k = \ln k_0 + \frac{\xi^2 Z_A^2}{2 \kappa T} \left(\frac{1}{D} - 1 \right) \left(\frac{1}{Y_A} - \frac{1}{Y_B} \right) - \frac{1}{\kappa T} \frac{\mu_B^2}{Y_B^2} \frac{D_0 - 1}{2 D_0 + 1} + \frac{\phi_A + \phi_B - \phi_M}{\kappa T} \dots \dots \dots (2)$$

$$\ln k'D = \ln k' + \frac{Z_A \mu}{D \kappa T Y^2 r^2} \dots \dots \dots (3)$$

where Z_A and Z_B are valencies of ions; r = radius of activated complex and T is the absolute temperature. In 1940, Laidler and Eyring gave the following equation for the reaction between ions and neutral molecules:

According to equation (2), $\log k$ varies linearly with $1/D$ at constant ionic strength. Amis and Jaffe gave an equation for the ion-dipole interaction which was modified later on by Amis as:

where $k'D$ is a function of dielectric constant D , Z_e is the charge on the ion, μ is the dipole moment of the dipole, k is the Boltzmann constant, T is the absolute temperature and r is the distance of approach for the ion and the dipole. Equation (3) predicts a linear relation between $\log k(\text{obs})$ and $1/D$. The slope of the line should be negative for a reaction between a negative ion and a dipole and positive for positive ion-dipole reactions. Laidler and Landskroener¹² developed the following general equation incorporating the corrections due to nonelectrostatic forces: In

$$\ln k = \ln k_0 + \frac{\xi^2 Z_A^2}{2 \kappa T} \left(\frac{1}{D} - 1 \right) \left[\frac{Z_A^2}{b_A} + \frac{Z_B^2}{b_B} - \frac{(Z_A + Z_B)^2}{b^2} \right] + \frac{3 \xi^2}{8 \kappa T} \left(\frac{1}{D} - 1 \right) \left(\frac{G_A}{b_A^2} + \frac{G_B}{b_B^2} - \frac{G^2}{b^2} \right) \dots \dots \dots (4)$$

Equation (4) also predicts a linear relation between $\log k$ and $(1/D)$.

In the acid hydrolysis of nitrophenyl esters¹³ in acetone-water mixtures, $\log k$ varied linearly with $1/D$ with negative slope instead of positive slope at all compositions for o-isomer and beyond 30% for p-isomer. These deviations with respect to the sign of their slopes may be attributed to the non-electrostatic interacting forces which are considerable at high concentrations of water. The variation of $\log k$ with $1/D$, for acetone-water mixtures is in qualitative agreement with the predictions of Laidler and Landskroener equation. The increase in rate constant with increase in dielectric constant can be ascribed to the formation of activated complex more polar than the reactants¹². Similar observations were made by Parausanu¹⁴ for acid hydrolysis of butyl acetate in acetone-water solutions and Laidler and

Landskroener for acid hydrolysis of amides¹². The high negative entropies of activation also suggest polar transition state complex¹⁵. A considerable decrease in entropy with addition of acetone or acetic acid and consequent change in the rate suggests the disturbance of the quasicrystalline structure of the aqueous environment, as was observed by Anantraman¹⁶ and Kudesia¹⁷.

Results and Discussion

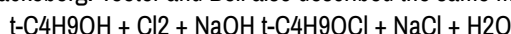
One of the prerequisites of the kinetic studies is the utmost purity of reagents and solvents, especially the redox reactions are highly sensitive to traces of impurity. Hence great care has been taken to secure and maintain the purity of the compounds and solvents used.

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 KMnO₄ solution.

Preparation of t-BuOCl

t-BuOCl was prepared by passing Cl₂ into cold aqueous sodium hydroxide and t-butyl alcohol (B.D.H.) as described by Chattaway Backeberg. Teeter and Bell also described the same method.



The hypochlorite was purified by distillation in an all glass apparatus, b.p. 80°C and stored in coloured bottles at about 0°C. Caution was exercised during preparation and separation to prevent exposure to strong light. It is a stable yellow liquid, having viscosity at 25°C = 0.543 centipoise²⁰ 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. AnalaR grade prechloric 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

The thermostat was controlled within $\pm 0.1^\circ\text{C}$. 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. The progress of reaction was studied idometrically at 35°C by estimating unreacted t-BuOCl 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 2 ml. of glacial acetic acid was added. The liberated iodine was titrated against standard sodium thiosulphate solution using freshly prepared starch as indicator²¹. 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. The studies have been carried out with varying concentrations of acetic acid.

Observations

In this paper the influence of solvent dielectric constant on the rate of oxidation of p-methoxybenzaldehyde and p-methylbenzaldehyde with t-BuOCl has been studied in various solvent mixtures of acetic acid and water. A summary of the experimental results is given in the following Table 1:

$k_0 \times 10^7 \text{ M sec}^{-1}$		
Medium Concentration	[p-methoxybenzaldehyde](a)	[p-methylbenzaldehyde] (b)
Water	5.4	4.6
10% Acetic acid	8.72	5.6
20% Acetic acid	13.2	6.75
30% Acetic acid	17.1	7.96
40% Acetic acid	28.1	11.6
50% Acetic acid	25.4	23.5
60% Acetic acid	20.6	19
70% Acetic acid	18.8	16.1
75% Acetic acid	16.1	13.5
80% Acetic acid	14.8	10
a = [t-BuOCl] = 0.0005M; [p-methoxybenzaldehyde] = 0.7000M; $\mu = 0.2$		
a = [t-BuOCl] = 0.0006M; [p-methylbenzaldehyde] = 0.2000M; $\mu = 0.2$		

Table 1: Effect of change of acetic acid concentration on the rate of oxidation of

p-methoxybenzaldehyde and p-methylbenzaldehyde with t-BuOCl at 35°C.

Conclusion

The results indicate that in the Oxidation of p-methoxybenzaldehyde with t-BuOCl the rate increases with increase in the percentage of acetic acid (from 10% to 40%). The rate is highest at 40% HOAc and with further increase in acetic acid content (50-80% HOAc) the rate decreases. But in the oxidation of p-methylbenzaldehyde with t-BuOCl the rate is maximum at 50% HOAc and decreases on either side of this percentage.

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