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Experimental Research of Kinetics Reaction of Alcohol NCSA in Water Acetic Acid

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Abstract: A study was analyzed “Experimental research of kinetics reaction of alcohol NCSA in water acetic acid.” The experimental research been examined by kinetic coordination by the second bromine molecule with the complex appears to be necessary for the removal of Br - ion from the complex as Br3- ion. In the halogen-addition to olefins in acetic acid reaction on $CH_2=CHCH_2C1$, $CH_2=CHOH_2CH$, and $CH_2=CHBr$. In the addition-reactions, the effect of added salts is to stretch the Br-Br2 bond in the transition state intermediate on Robertson et.al., found, from their kinetic study of Bromine and add to various elements olefins in aceti-acid, that’s overall reactions are 3rd-order (first-order in olefin and second-order in bromine) even in fairly dilute solutions of reactants.

Keywords: Chemical kinetic, NCSA, Bromine-addition, Acetic acid and ion

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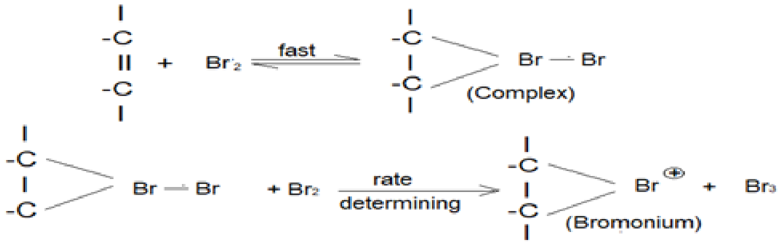
INTRODUCTION

than 1%, as compared to 4% reported by earlier workers.

Mechanism in Acetic Acid: Robertson et. al., studied the kinetics of Bromine-addition with various substituted olefins observed third-order kinetics (first-order in olefin and second-order in bromine) even in fairly dilute solutions of reactants. They suggested a mechanism in which there is a primary formation of a complex between olefin and bromine. The complex then reacts with another molecule of bromine to give bromonium-ion.[2]

The scheme is as follows:



This mechanism well accounts for the formation of bromonium ion and hence, trans-addition. The coordination by the second bromine molecule with the complex appears to be necessary for the removal of Br^- ion from the complex as $Br3^-$ ion. In the halogen-addition to olefins in acetic acid, response rules related to bromine are two whereas related order to chlorine are always unity. The reason may be that the tribromide anion, $Br3^-$, is quite stable in acetic acid whereas the trichloride anion, $C1^-3$, is not.

Effect of Added Salts in Acetic Acid Medium:

This aspect of the problem has been investigated both for bromine-addition to olefinic compounds and for aromatic bromine substitution and somewhat similar conclusions have been reached.

For a reaction between dipolar molecules, Hughes and Ingold proposed that the difference in charge distribution in the initial and transition states determines the direction of change in reaction rate with changes in medium. A reaction for state is more polar than the reactants will be favoured by increasing the ionizing powers of the middle order, either this addition of a solvent of greater ionizing power or by the addition of salts. In acetic acid medium, the rate of aromatic bromination and bromine-addition to reaction for which the transition olefins have been found to increase, with the addition of water (which is more polar than acetic acid) or salts to the medium. The reaction involves dipolar, but neutral molecules of substrate and bromine. Therefore, according to the view of Hughes and Ingold the transition state of the reaction should be more polar than the reactants. In the addition-reactions, the effect of added salts is to stretch the Br-Br2 bond in the transition state intermediate.[3] But, substitution process includes also the stretching of C-H bond with subsequent proton release. Hence, the activity of the added electrolytes is less for addition than for substitution Also, the effect is more pronounced for chlorination than for bromination, which has been attributed to the greater ionising power of chlorine.

A added halide ion, in the molecule second bromine molecule with the complex appears to be necessary for the removal of Br^- ion from the complex as $Br3^-$ ion. The rate expression for the intervention of an ion in the kinetics of the reaction may be represented by:

$$\frac{-d\,[Br_2]}{dt} = k\ [S]\ [C1^-] \text{ or } \frac{-d\,[Br_2]}{dt} = k\ [S]\,[Br^-] = k\ [s]\ [Br_3^-],$$

Were, S is the olefinic substrate. With excess of bromide ion, the reaction reaches a maximum rate when substantially all the bromine has been converted into $Br3^-$ ion. Comparison of the effects with these structures from the rate of bromine addition by this mechanism in acetic-acid 25ºC is as follows:

Compound	--	--	--	**$CH_2=CHCH_2C1$**	**$CH_2=CHOH_2CH$**	**$CH_2=CHBr$**
Rate (Br_2)	--	--	--	01.6	00.23	.001
Rate	(Br_2+M/20 LiCl		--	10.00	02.40	.007

Since on reagent boths in this catalyzed in uncatalyzed reaction's must be powerfully electrophilic in character, and unlike acetic-acid that from of catalyses involved that ions i.e., $Br_2\ 01^-$.[4]

The introduction of $-CH_201$ group into ethylene reduces the rate bromine-addition relative to that for ethylene by a factor of 12. In this, the $-CH_2Cl$ group trends to hinder the anionization of a bromine atom from the intermediate. The chloride ion in the added eatalyed (LiCl) first attaches itself on the r-carbon atom by a nucleophilic attack resulting in the formation of ionic intermediate,

$$ClCH_2 — CH — CH_2Cl$$

The ions formed in this way are susceptible to electro-flame attacks by the bromine due to their negative load.[5]

The presence of substituents activating the ethylenic linkage diminished the relative influence of external catalysts. The ratios of lithium chloride (N/20) catalyzed reactions to the unestalysed reaction in acetic acid at 24ºC for allyl-chloride and interred r phenyl derivative are:

$CH_2 = CHCH_2Cl$
6.3

$PhCH = CHCH_2Cl$
1.3

In the r-phenyl derivative, the positive charge on the r-carbon atom is reduced due to the tautomeric displacement through the phenyl group. This lessens the attack by chloride ion, and hence, the lower ratio.

LiCl is usually chemical formula better catalyst then LiBr. If water is added to the solvent, the anion catalyzed reaction is eliminated as the enhanced solvation of the halide ions reduces their nucleophilic reactivity. Compounds such as acid chlorides do not have acid catalysts. Chloride salts do not have a basic group that attracts protons.[6]

Most motion data checked at kinetic top of halogenic to unsaturated substances refers to organic solvents. Acetic acid and carbon tetrachloride. Testing halogen additions, especially in powerful polar (Br2 Brz, also HOBr.) media in aqueous solutions, involves much faster reactions, but has the advantage that the concentration of active halogen species is accurately predictable and controllable.

Kanyaer 1945 studied the bromine-addition to some olefins in aqueous solution. Kanyaev has been tested. This included highly negative substituents needed to maintain a sufficiently slow reaction.[7] This study reported that the relative reactivity of tribromidion and molecular bromines differed significantly from one to one. The olefin and its relative reactivity was related to the proportion of wetting of the product dibramide and bromine, provided that the former was produced by the reaction of bromine and water by the reaction of tribromidione with tribromidione. This assumption is comparable to the reaction scheme proposed by Hine, The body is formed which forms at the equilibrium stage and combines the addition complex and reaction with bromine or water at the velocity step of the olefin velocity step at the equilibrium step.[8]

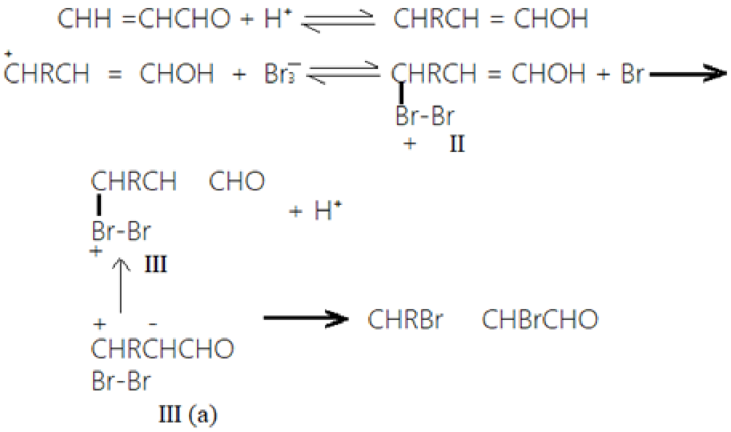
Atkinson and Bell using electrometric methods, Atkinson and Bell investigated the kinetics of the bromuolofin reaction in aqueous solutions. The reaction is assumed to contain corkunium ion intermediates formed by the reaction of olefins with Br_2 or Br3, followed by a rapid reaction of the intermediates with water or bromide ions.[9]

Nucleophilic Bromine-Addition:

Ingold and Ingold predicted that nucleophilic halogen-addition is possible with olefinic-compound containe sufficiently strong electron on the demandable group, the reactions of α, ß- unsaturated aldehyde's and ketone's inside acetic-acid 28,58. The addition on the Br too cinnamaldehyde is rapid in presence of perchloric acid. But the catalysis is suppressed by the addition of water. The catalytic activity of acids lies in the order:

Perchloric > sulphuric > nitric

So, this catalytic activity is very rapid addition to unsaturated aldehydes and ketones compared to acids, suggests that addition are initiate by nucleophilic-halogen. However, this initial-polarization towards olefin by the electron-demanding power of the substituents isn't the any one factors and its concerned within determined Psn rate, further the spite on greater's electron with drawing power to the nitro group, -nitrostyrene is less reactive than cinnamaldehyde in acid-catalysed reactions. Nozaki and ogg,[10] by studying bromine-addition to maleic acid, showed that in such an acid catalysed reaction, the proton plays a specific role. As a catalyst, hydrobromic-acid is higher impacts and effective on LiBr. In other words, the rate of addition depends on the basicity of the electron-withdrawing group, that is, the capacity to accept and accommodate the proton. It involves nucleophilic attack by halogen molecule or by a tribalide ion when acids are present. The bindings for catalytic stage of the catalytic stage at the additional level of the catalytic level involves nucleophilic attack by halogen molecules (or via tribal analysis if there is an acid) as shown below-



In the addition of bromine, catalysed by hydrogen bromide, to acrylic acid, it is found that the rate increases to a maximum value with added hydrogen ions and then decreases. A similar effect is generally observed with bromine and added acids. The reason is that large concentrations of hydrogen ions will maintain a proton in the intermediate-II and make addition unfavourable.[11] The proposed mechanism also explains the reduction in catalyzed rate addition form Br^- acid by the added water to the solvent acetic acid. Water reacts on H+base and greater stability of H_2O also H_2OAc. The protons that form reactive intermediates are not readily available.

CONCLUSION

The point of view of the kinetic collision theory. it is known that truly termolecular reactions rare. However, Robertson was found a kinetic study of bromine addition to various substituted olefins in acetic acid, that overall reaction is of the third order (first-order in olefin and second-order in bromine) even in fairly dilute solutions of reactants. The first stage is the association of bromine molecule with olefin to form a complex. This fast reaction is followed by interaction of the complex with another ‘bromine molecule’ to form bromonium ion and tribromide anion. The bromonium - ion, then, fastly reacts with the bromide ion resulting in the formation of the dibromide (final product). Akinetic study has been made on the bromination of four vinyl compounds, namely, acrylamide, meth acrylamide, n-butyl methacrylate and crotonic acid and acetic acid. In all the compounds, electron-demanding groups are present. The reactions are very slow and total third- order kinetics has been observed. Although the mechanisms cited above for the third-order bromine-addition well account for the observed results, according to the writer, there is need for modification of the mechanism, especially with regard to the structure of the -complex and the mode of attack of the second bromine molecule on this complex.

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