



Iodination of aroyl Ketene Dithioacetals Derivatives by Iodine and Iodic Acid with its kinetics

Girish Deshmukh, Sarla Kalyankar*, Mohan Kalyankar

P.G. Research Center Department of Chemistry Yeshwant Mahavidyalaya Nanded-431602.
Maharashtra. (INDIA)

E-mail : girish.deshmukh2@gmail.com

Abstract

The iodination kinetics of the substituted α - aroyl ketene dithioacetals derivatives using iodine and iodic acid with ethanol has been studied under different conditions. The rates are first order kinetics in iodine and α - aroyl ketene dithioacetals and zero order with respect to iodic acid. The rates of reactions are measured at different temperature and activation parameters for all these.

Keywords:- α -aroyl ketene dithioacetals, iodine, iodic acid, Ethanol, Kinetics.

1. Introduction

To study the kinetics of these organic compounds number of reagents such as molecular iodine ,iodine monochloride, N-iodosuccinimide have been used¹⁻³. But most of reagents used are toxic, expensive and generates hazardous waste .While the only iodine and iodic acid an efficient solid iodinating agent which has no hazardous effect and ecofriendly⁴⁻⁵.The kinetic study of iodination of these compounds has been the subject of numerous studies due to the potential of the product to serve as intermediate in different organic synthesis⁶. Iodination of aromatic rings is an electrophilic substitution reaction with wide applications in organic synthesis especially in the synthesis of pharmaceutical products⁷⁻⁸. Aromatic iodides have been used in the synthesis of so many different natural products and also as bioactive products⁹. They also have importance in medicinal and pharmacological research¹⁰.

Chemical kinetics used for the

determination of the rate and order of the reaction in terms of concentration of reactants and other parameters¹¹⁻¹³. Therefore kinetic study of the reactions is real analysis for a chemist to investigate the processes whereby a system is transformed from one state to other and a work out the controlled conditions required for gaining a desired product on a commercial scale¹⁴⁻¹⁵. Thus kinetics can also be termed as chemical dynamics. This Chemical kinetics helps in studying the mechanism of reaction which occurs in several stages, which are not given by stoichiometry¹⁶. The presence of these stages may be searched by a complete picture of reaction involving the equilibrium state. This involves the complexities where others postulations have to be made and consequently the applications becomes very difficult. Most important point is primary reactants and the products of slow step in a reaction sequence can not be detected by kinetic result, but they can be detected by the knowledge of empirical formula of the activated complexes¹⁷⁻¹⁸. The nature of

reactions and identification of the products will provide evidences for mechanism when the reaction will attain the equilibrium state rapidly before the slow step. In coming years, iodoaromatic compounds have assumed increasing importance in organic synthesis because, iodine being more reactive than their respective bromides and chlorides¹⁹⁻²⁰. Moreover they are able to form a large variety of stable aromatic polyvalent iodine compounds, which have found increasing significance in modern synthesis procedure²¹⁻²².

2. Materials and Methods

Kinetic measurements:

The reactions were carried out under pseudo first order conditions by keeping an excess of substrate over, iodine and iodic acid. The progress of reaction was followed by estimating the concentration of unreacted iodine spectrophotometrically at wavelength 545 nm. The rate constants were determined by least square method, from the linear plots of log OD versus time.

Stoichiometry and product analysis:

Stoichiometry of iodine and iodic acid and α -aroyl ketene dithioacetals reaction was determined by allowing the reaction mixture containing substrate, iodine and iodic acid in 5:2:1 molar ratio in ethanol to go to completion at room temperature. Then the reaction mixture was poured in water to get solid product. The iodinated product was analyzed using preparative TLC on silica gel, and comparing the melting point of product with the known sample.

3. Results and Discussion

The results of iodination of substituted α -aroyl ketene dithioacetals by iodine and iodic acid are presented in table 1-4.

Effect of variation of [substrate]:

At constant [Iodine] and [Iodic acid], the increase in [substrate] enhances the reaction rate. The plot of $\log K_{obs}$ versus \log [substrate] for different initial concentration of substrate is linear with unit slope indicating the first order dependence on substrate (table-1).

Table 1: Effect of Variation of [substrate] on Reaction Rate

Substrate	$K_1 \times 10^4 \text{ sec}^{-1}$					
	4- OCH ₃	4- NO ₂	4-Br	4- Cl	4-F	4-H
0.0040 M	4.01	4.14	3.76	3.97		3.54
0.0035M	3.81	3.97	3.49	3.68		3.32
0.0030M	3.03	3.21	2.86	2.95		2.77
0.0025M	2.68	2.79	2.40	2.54		2.28
0.0020M	2.49	2.58	2.27	2.36		2.19

[Iodine]= 0.004 M, [Iodic acid] = 0.004 M, Temperature = 301K, Solvent = Ethanol

Table 2: Effect of Variation of [Iodine] on Reaction Rate

Iodine	$K_1 \times 10^4 \text{ sec}^{-1}$					
	4- OCH ₃	4- NO ₂	4-Br	4- Cl	4-F	4-H
0.0040 M	4.28	4.14	4.01	3.97	4.28	3.54
0.0035M	4.11	3.89	3.77	3.64	4.07	3.27
0.0030M	3.41	3.30	3.01	2.88	3.38	2.62
0.0025M	2.94	2.66	2.53	2.42	2.82	2.30
0.0020M	2.63	2.48	2.41	2.37	2.69	2.08

[Substrate]= 0.004 M, [Iodic acid] = 0.004 M, Temperature = 301K, Solvent = Ethanol

Table 3: Effect of Variation of [Iodic acid] on Reaction Rate

Iodic Acid	$K_1 \times 10^4 \text{ sec}^{-1}$					
	4- OCH ₃	4- NO ₂	4-Br	4- Cl	4-F	4-H
0.0040 M	3.63	3.97	4.02	3.92	4.13	4.14
0.0035M	3.33	3.64	3.84	3.80	4.12	3.87
0.0030M	3.48	2.88	3.97	3.74	4.21	3.01
0.0025M	3.09	2.42	3.56	3.38	4.60	2.53
0.0020M	3.08	2.37	3.23	3.18	4.33	2.41

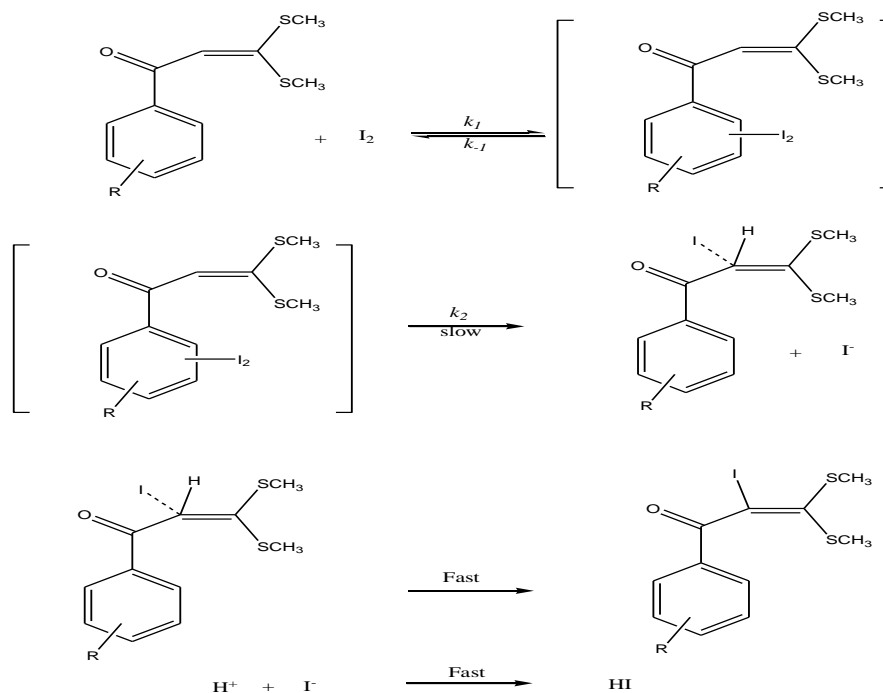
[Substrate]= 0.004 M, [Iodine] = 0.004 M, Temperature = 301 K ,Solvent = Ethanol

Table – 4 Rate Constant of Iodination of α - aroyl ketene dithioacetalsby Iodine and Iodic Acid at Different Temperature

Sr. No.	Temperature	301	306	311	316	321
	Substrate	$K_1 \times 10^4 \text{ sec}^{-1}$				
1	4- OCH ₃	4.36	4.77	5.36	6.02	7.84
2	4- NO ₂	4.01	4.52	5.03	5.87	7.73
3	4-Br	3.89	4.29	4.85	5.22	7.26
4	4- Cl	3.78	3.97	4.71	5.16	7.00
5	4-F	3.54	3.71	4.64	4.99	6.91
6	4-H	3.10	3.25	4.38	4.91	6.86

[Substrate]: 0.004M, [Iodic Acid]: 0.004M, [Iodine]: 0.004M, Solvent: Ethanol

Mechanism of Iodination of Hydroxy Aromatic Ketone by Iodine and Iodic Acid:





Effect of variation of [Iodine]:

At constant [Substrate] and [Iodic acid], the increase in [iodine] enhances the reaction rate. The first order plots of log OD versus time were linear. The plot of log k_{obs} versus log [Iodine] for different initial concentration of iodine is linear with unit slope indicating the first order dependence on iodine (table-2).

Effect of variation of [Iodic acid]:

At constant [substrate] and [Iodine], the increase in [Iodic acid] did not affect the rate of reaction. The pseudo first order rate constants computed from the plots remained unaffected by the change in [Iodic acid], establishing the zero order dependence of the rate on iodic acid in all cases (table-3).

Effect of temperature:

The study of iodination of different α - aroyl ketene dithioacetal has been subjected to different temperature range 301 K to 321 K by keeping the concentration of substrate and

reagent constant. The rate constants are given in (table 4).

4. Conclusions In summary, kinetic study of iodination at different concentration of substrate, iodine and iodic acid is given, from that we can conclude there is difference in values of rate constants when we change substrate and iodine concentration as shown in table 1 and 2 but no effect on rate constant value when there is change in concentration of iodic acid as in table 3. Increase in temperature will increase value of rate constant as in table 4.

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6. References

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