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NUCLEOPHILIC SUBSTITUTION REACTIONS OF 2, 4-DINITTROPHENYL ACETATE WITH HYDRAZINE AND METHANOL SOLVENT EFFECT

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Abstract:-

The generally accepted mechanism for nucleophilic aromatic substitution (the snare mechanism) is an additionelimination mechanism and involves the formation of a Meisenheimer type of intermediate. The hydrazinolysis of 2,4dinitrophenyl acetate in methanol proceeds exclusively through acyl-oxygen scission by a concerted mechanism. The process depends on the basicity of the leaving group and its steric hindrance as well as the possible intramolecular hydrogen bond in the transition state. The reactions of 2,4Dinittrophenyl Acetate with hydrazine obeyed pseudo-firstorder rate constants (k_{obs}). The linearplot of k_{obs} vs. amine concentration indicated that there is no base-catalysis.The large negative $\Delta S^{\#}$ value indicates a rigid transition state or great participation of methanol molecules in the activated complex.

Keywords: - *2, 4-Dinittrophenyl Acetate, methanol Solvent, Hydrazine and Nucleophilic*

INTRODUCTION

Nucleophilic aromatic substitution reactions on aromatic compounds able to stabilize radical anions, such as dinitrobenzenes, nitrobenzophenones, nitrobenzonitriles, polyfluoronitrobenzenes, etc.,show normally radical features. However, radical anions of those compounds are stable toward dissociation and except for the very particular case of oiodonitrobenzene [1] no example of the SRN~ chain mechanism [2]One interpretation, proposed to justify the radical features of the reactions of dinitrochlorobenzenes with hydroxide ion, suggests the intermediacy of radical anions, formed through electron transfer from the nucleophile to the substrate [3]The generally accepted mechanism for nucleophilic aromatic substitution (the S_NAr mechanism) is an addition-elimination mechanism and involves the formation of a Meisenheimer type of intermediate[4]. The rate-limiting step is EPH - International Journal of Applied Science | ISSN: 2208-2182 23 the formation of the intermediate, the expulsion of the leaving group, or the proton transfer process. Several properties of the nucleophiles (basicity, polarisability, degree of solvation, etc)or leaving groups more or less influence reactivity depending on the kind of interaction between nucleophile, leaving group, substrate and solvent[5]

In reactions in which bonds are broken, part of one reactant, the leaving group, becomes detached. Actually, one might expect that a good leaving group gives an increased rate of substitution, whatever substrate or nucleophile is involved. Therefore, the leaving group can determine reactivity in nucleophilic substitution in aromatic system. This has fostered the illusion that the leaving group ability depends upon the pK_a of the conjugate acid of the leaving group and will affect the rate of reaction if the leaving group is involved in the ratedetermining step [6] strongly supported the hypothesis of a two-step pathway for nucleophilic aromatic substitution, using as a criterion the so-called "element-effect" i.e., the variation in the rate of substitution as a leaving group is varied. To gain further understanding of the mechanism for nucleophilicaromatic substitution, and in order to explain the mobility of the leaving groups and substituent containing leaving group, kinetic studies of hydrazinolysis of 2,4-dinitrophenyl acetate With Hydrazine in methanol solvent

MATERIALS AND METHODS

GR grade MeOH were spec pure and commercially available, GR grade, was used after distillation. GR grade, hydrazine 99% was used without furtherpurification.

Preparation of Substrates: 2, 4-Dinittrophenyl Acetate [7]

Wasprepared by refluxing2, 4-dinitrophenol with excess acetic anhydride for 3 hours. The reaction mixture was workedup with water,extracted with methylene chloride and dried over anhydrous MgSO4, and the product was crystallized frommethanol as pale yellow needles, m.p. 69-75 °C

Product Analysis A mixture of the desired 2, 4-Dinittrophenyl Acetate (X = OCOCH3) (0.05 mile) and hydrazine (0.5 mile) in methanol were stirred at room temperature. The formed precipitate was filtered, washed with cold methanol and recrystallized from methanol. Analysis of the products gave a mixture of 2, 4-dinitrophenol and acetyl hydrazide.
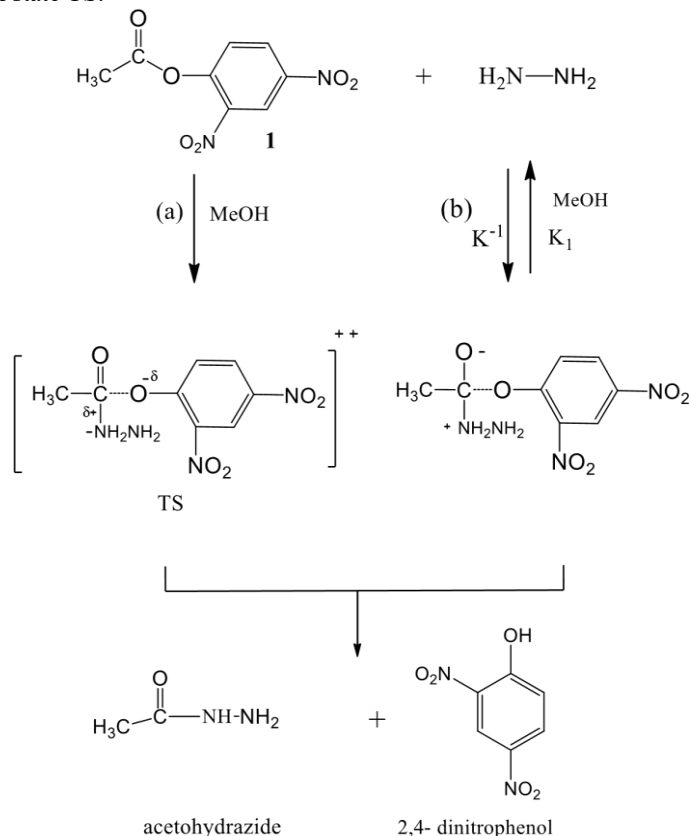
RESULTS AND DISCUSSION

It has long been known that either the acyl-oxygen bond or aryl-oxygen bond of phenyl esters can be cleaved depending on (i) the structure of the ester[8], (ii)the nature of reagent[9], (iii) the basicity of the leaving group anion from the ester compared to that of the attacking 24 nucleophile(iv) the nature of substituent in the non-leaving or leaving group containing the ester[10], and (v)the relative "hardness" and "softness" of the reaction site and reagent[11]We studied the mechanism for the reaction of 2,4-dinitrophenyl acetate with hydrazine in MeOH to examine the mode of scission whether through the CO-O or/and Ar-O bond scission pathways. The reaction in methanol proceed exclusively through acyloxygen scission rather than aryl-oxygen scission as indicated from the isolation and identification of acetate hydrazide, 2, 4-dinitrophenoxide, Scheme 1. Furthermore, the exclusive acyl-oxygenfission is attributed to the fact that the departure of 2, 4-dinitro-phenoxide is better than the acetate as a leaving group. This is consistent with the fact that acetic acid is a relatively stronger acid with pKa = 9.57 (MeOH)[12]where 2,4-dinitophenol pK_a value is equal 7.83 (MeOH)[13].The reactions of 2,4-Dinittrophenyl Acetate with hydrazine obeyed pseudo-first-order rate constants (k_{obs}). The linear plot of k_{obs} vs. amine concentration indicated that there is no base-catalysis and the overall reactions follow the route given by Scheme1. The large negative $\Delta S^{\#}$ value indicates a rigid transition state or great participation of methanol molecules in the activated complex [14], Table 1.

Table 1. Second-order rate constants, k_N(l mol^{-1}s^{-1}), for the reaction of 2,4-dinitrophenyl acetate with hydrazine in methanol at different temperatures

Amine/T°C	10	15	20	25	30	- $\Delta S^{\#}$ Jmol^{-1} K^{-1}	$\Delta H^{\#}$ K Jmol^{-1}
Hydrazine	11.50	12.11	12.69	13.28	13.81	228.89	6.44

Suggested that the leaving group departs slowly in either a concerted mechanism, scheme 1, pathway (a) or a stepwise mechanism, Scheme 1, pathway (b). They chose to favor a step wise mechanism. However, our results could favor a concerted mechanism rather than a stepwise mechanism because i)intramolecular hydrogen bond is not preferred in polar solvents and the large negative $\Delta S^{\#}$ value are in the line with concerted mechanism or the break-down of the addition intermediate to the products is the rate determining step,(ii) the pK_a of the conjugate acid of the leaving group (2,4dinitrophenoxide ion) is 7.83 while the pK_a value of hydrazine is 8.10 respectively[15] It is apparent that the basicity of the incoming amines and the basicity of the leaving group are approximately the same, Scheme 1, pathway (a). Therefore, we can propose that the hydrazinolysis of 2,4-Dinittrophenyl Acetate in MeOH proceeds through a concerted mechanism with a transition state TS.

Scheme 1. The reaction possible mechanism of 2, 4-dinitrophenyl acetatewith hydrazine in MeOH

The kinetic studies were measured spectrophotometrically. Fig (1) show the spectrum at interval times for the reaction of 2,4-Dinittrophenyl Acetatehydrazine in MeOH respectively. The reactions of 2,4-dinittrophenyl acetate with hydrazine obeyed pseudo-first-order rate constants (k_{obs}) which were obtained from the slope of the linear plot of in ($A_\infty - At$) vs. time.
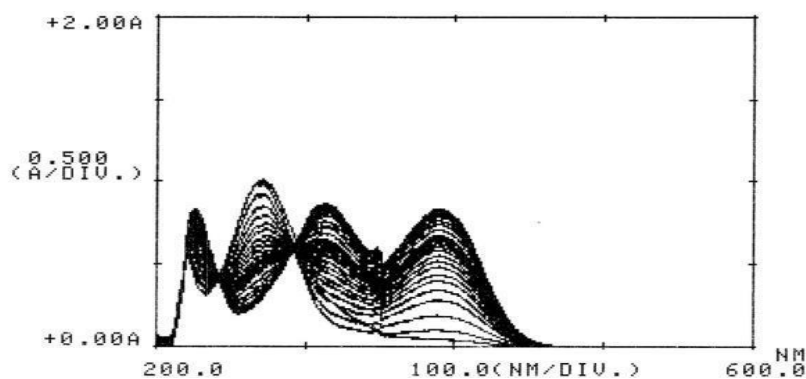

Fig (1): Full spectrum for the reaction of 2,4-dintrophenylacetate with hydrazine in MeOH

CONCLUSION
The reaction of 2,4-dinitrophenyl acetate with hydrazine in MeOH proceeds exclusively through acyl-oxygen scission. The reaction obeyed pseudo-first-order rate constants (k_{obs}) and the large negative $\Delta S^{\#}$ value indicates a rigid transition state or great participation of methanol molecules in the activated complex. The leaving group departs slowly in a concerted mechanism due the large negative $\Delta S^{\#}$ value, the lower value of the pK_a of the conjugate acid of the leaving group than that of the hydrazine, and the basicity of the incoming amines and the leaving groups are the same.

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