

Kinetics of Periodate Oxidation of Aromatic Amines: Studies on the Kinetic Parameters and Isokinetic Relationship for Few Anilines

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Various kinetic parameters for the periodate oxidation of anilines, viz. aniline, *p*-ethylaniline, *o*-ethylaniline, *p*-chloroaniline, *p*-bromoaniline, *p*-methoxyaniline, *p*-ethoxyaniline, *m*-methylaniline and *p*-methylaniline in acetone-water medium have been reported and discussed. The validity of isokinetic relationship has been tested for finding out some of the informations related to the mechanism of this reaction series. The isokinetic temperature has been evaluated and discussed. The results have been found to differ from the earlier reported work.

INTRODUCTION

Various kinetic parameters are used for making important revelations about the transition state, its solvation and the role of solvent in the mechanism of a reaction. The isokinetic relationship¹ is also an important tool for deciding the nature of mechanism. The validity of this relationship is suggestive of the similar mechanism for the reaction series under consideration. Srivastava *et al.*² studied the isokinetic relationship and reported the kinetic parameters for the periodate oxidation of six anilines in 15% acetone-water medium, taking the anilines in excess and reported the value of isokinetic temperature β as 278 K. Rao *et al.*³ reported a very high value (666 K) for β in methanol-water medium. The reported studies are contradictory and therefore the periodate oxidation of more anilines should be undertaken to get a more clear picture. Further, the studies may be made by taking the oxidant in excess. Therefore we have undertaken the studies related to kinetic parameters and isokinetic relationship for the periodate oxidation of nine anilines. viz., aniline, *p*-ethylaniline (PEA), *o*-ethylaniline (OEA), *p*-chloroaniline (PCA), *p*-bromoaniline (PBA), *p*-methoxyaniline (PMOA), *p*-ethoxyaniline (PEDA), *m*-methylaniline (MMA) and *p*-methylaniline (PMA), in 10% (v/v) acetone-water medium and taking the periodate in excess.

EXPERIMENTAL

All chemicals used were of BDH/Loba GR or E. Merck grade and were used after recrystallization or redistillation. Doubly distilled water was used for preparation of solutions and the reaction mixtures.

The reactions being quite fast were studied in 10% (v/v) acetone-water medium and in absence of any catalyst. Because of the formation of colored products, the progress of reaction was followed by recording the absorbance at different λ_{\max}

of the reaction mixtures at different intervals of time on Shimadzu double beam spectrophotometer (UV-150-02). Studies were kept confined only to the period in which the λ_{\max} of the reaction mixtures did not change. The λ_{\max} for reaction mixtures of aniline, PEA, OEA, PCA, PBA, PMOA, PEOA, MMA and PMA have been found to be 355 nm, 480 nm, 520 nm, 430 nm, 450 nm, 475 nm, 485 nm, 540 nm and 470 nm respectively.

RESULTS AND DISCUSSION

These reactions were found to follow second order kinetics being first order in each reactant. The reactions were studied under pseudo first order conditions taking periodate in excess and the Guggenheim method⁴ was employed for reporting the pseudo first order rate constants which were divided by the concentration of periodate to get the second order rate constants K_2 . It should be noted that the initial rates have been used by Srivastava *et al.*² for testing the validity of isokinetic relationship and for evaluation of the kinetic parameters for the periodate oxidation of comparatively fewer anilines and that it is always better to use the rate constants for such studies as has been done by us.

The reactions were studied at four temperatures to evaluate various kinetic parameters *viz.* E_a , ΔF^\ddagger , ΔS^\ddagger and ΔH^\ddagger . The Arrhenius equation⁵ was found to be followed for each aniline studied. The various activation parameters as evaluated on the basis of the Arrhenius plots (Fig. 1) are recorded in Table-1.

TABLE-1
KINETIC PARAMETERS FOR DIFFERENT ANILINES

Aniline	E_a (Kcal mol ⁻¹)	ΔF^\ddagger (Kcal mol ⁻¹)	$-\Delta S^\ddagger$ (E.U.)	ΔH^\ddagger (Kcal mol ⁻¹)
Aniline	8.66	20.86	41.34	8.04
PEA	5.68	20.94	51.18	5.06
OEA	3.63	20.54	56.47	3.15
PCA	4.33	20.63	54.53	3.71
PBA	7.41	21.31	46.79	6.78
PMOA	4.21	19.44	50.19	3.60
PEOA	7.42	19.19	39.88	6.81
MMA	8.46	20.45	52.30	7.86
PMA	8.64	19.58	36.94	8.03

A perusal of the data in Table-1 clearly indicates that these reactions are characterized by a low value of the energy of activation, E_a , and a large negative value for the entropy of activation, ΔS^\ddagger . The high negative value of ΔS^\ddagger suggests the formation of a charged and rigid transition state, which is expected to be strongly solvated. The low value of energy of activation is of the order of the value for bimolecular reactions in solution. Since the reactions are of the ion-dipolar type^(2, 3, 6-8), it is expected that the ΔS^\ddagger for all anilines should be nearly of the same order of magnitude suggesting thereby the involvement of solvent in

the mechanism. However, because of differences in the polarity of different anilines, the extent of solvation may be different and so the experimental value of ΔS^\ddagger may be different for different anilines as observed by us. Further the free energy of activation, ΔF^\ddagger and the activation energy is of a comparable order of magnitude, suggesting that the mechanism for these anilines should be similar.

To test the validity of the isokinetic relationship¹, a plot of ΔS^\ddagger vs ΔH^\ddagger was made (Fig. 2). This plot was found to be linear (correlation coefficient being 0.97) showing that the isokinetic relationship is being followed. The value of isokinetic temperature, β , was found to be 273.27 K. A linear relationship between ΔS^\ddagger and ΔH^\ddagger suggests that the same interaction mechanism may be followed in the oxidation of these anilines. However, it may be worthwhile to point out that a high correlation coefficient does not always mean that the basis for the relationship is the presence of a single interaction mechanism⁹. A straight line may be obtained even in the presence of two interaction mechanisms if their β values happen to be equal. In spite of this uncertainty employed, it is reasonable to assume in this case that the same interaction mechanism is probably being followed as other kinetic features go to support this conclusion.

The value of β evaluated by us is quite small in comparison to that reported by Rao *et al.*³ At the temperature above β , the reaction rate or equilibrium is controlled mainly by ΔS^\ddagger . As the experimental temperature range used by us is much higher than the β value, these reactions may be considered as entropy controlled. This conclusion is also contradictory to the findings of Rao *et al.*³

On the basis of the foregoing discussions and our earlier work⁶⁻⁸ it may be assumed that the periodate ion attacks the nitrogen of anilino group in a slow step and forms a transition state having stabilization of positive charge on the nitrogen. This transition state should be attacked by the water molecule to give products in a

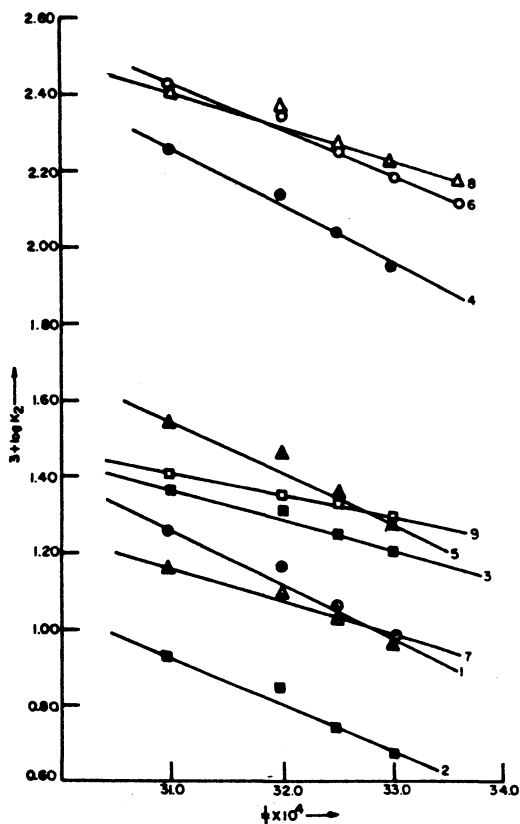


Fig. 1 Arrhenius plots (1) Aniline, (2) *p*-bromoaniline (3) *p*-Chloroaniline (4) *p*-toluidine (5) *m*-toluidine, (6) *p*-ethoxyaniline (7) *p*-ethylaniline (8) *p*-methoxyaniline

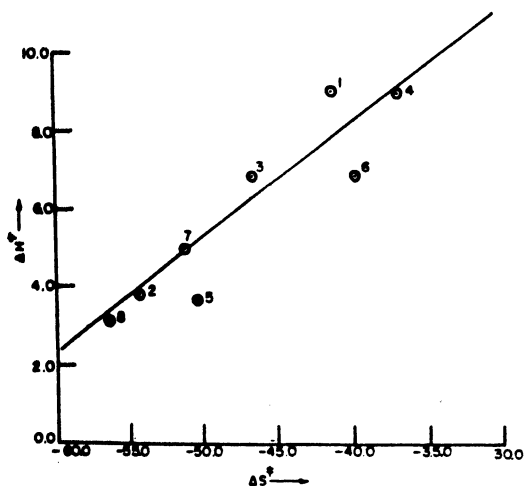
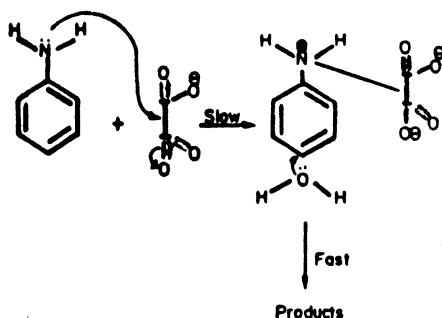


Fig. 2 Isokinetic relationship
 $\beta = 273.27^\circ\text{A}$ (1) H, (2) *p*-Cl, (3) *p*-Br, (4) *p*-CH₃, (5) *p*-OCH₃, (6) *p*-OC₂H₅,
 (7) *p*-C₂H₅, (8) *o*-C₂H₅

fast process (Scheme I). However, the site of attack of the solvent molecule and the products of reaction may depend on the substituents present in the aniline nucleus.



Scheme-I

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