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THERMODYNAMIC AND LFER STUDIES FOR THE OXIDATION OF ANILINES BY THE PERIODATE ION

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ABSTRACT

The various thermodynamic parameters for the periodate oxidation of six anilines, viz. aniline, *p*-chloroaniline, *p*-ethoxyaniline, *o*- and *p*-methoxyanilines and *p*-methylaniline have been reported and discussed. The validity of the isokinetic relationship and various linear free energy relationships (LFERs) have been tested and discussed. An attempt has been made to correlate these findings with the mechanism operative in these reactions.

INTRODUCTION

One of the important tools in deciding the mechanism of reactions is the study of substituent effects and thermodynamic parameters. The Hammett equation and its modified forms [1], all known as linear free energy relationships (LFERs), have been found useful for correlating reaction rates and equilibrium constants for side-chain reactions for *meta* and *para*-substituted benzene derivatives. These relationships are based on an important generalization that reactions of a particular reaction series follow a similar mechanism. The isokinetic relationship [2] is also an important tool for deciding the nature of a mechanism. Occasionally, differences in the activation energy have been used as evidence for a change in reaction mechanism. A literature review on periodate oxidation revealed [3] that no attempt has been made to correlate rates with different LFERs and no study has been made to discuss the effect of various thermodynamic parameters on the mechanism for the oxidation of monosubstituted anilines. Keeping this in view, a systematic study of various LFERs and the isokinetic relationship has been made to establish the role of substituents and to decide the nature of the mechanism (radical or ionic) being followed in the periodate oxidation of anilines. The results of these studies are presented and discussed in this paper.

TABLE 1

λ_{max} values of the reaction mixtures for different anilines
Temp., 25°C; medium, 15% acetone in water (v/v).

Aniline	λ_{max}(nm)
Aniline	355
p-Chloroaniline	430
p-Methylaniline	480
o-Methoxyaniline	510
p-Methoxyaniline	470
p-Ethoxyaniline	460

EXPERIMENTAL

Materials and Methods

Sodium metaperiodate (M & B AnalaR grade) was used after recrystallization and the different anilines (B.D.H./Aldrich) were used after redistillation or recrystallization. All other chemicals used were of AnalaR or G.R. grade. Doubly distilled water was used for preparation of solutions.

Because of the formation of coloured products, the progress of the reaction was followed by recording the absorbance at different λ_{max} (recorded in Table 1) of the reaction mixture at different intervals of time on a B and L spectronic-20 spectrophotometer. Studies were confined to the early stage for which the λ_{max} value of the reaction mixture in each case did not change. Kinetic runs were carried out in a 15% acetone–water medium.

These reactions were found to follow second-order kinetics, being first order in periodate and first order in anilines as evaluated by the van't Hoff differential method. These reactions were studied under pseudo-first-order conditions (taking anilines in excess) and initial rates (dA/dt) in terms of rate of absorbance change were evaluated by the plane mirror method [4]. The second-order rate coefficients (obtained by dividing the initial rates by the concentration of the aniline employed) thus obtained were utilized to evaluate various thermodynamic parameters and to study various LFERs.

RESULTS AND DISCUSSION

Thermodynamic parameters and validity of the isokinetic relationship

The reactions were studied at different temperatures to evaluate various thermodynamic parameters. The Arrhenius equation [5] was found to be followed for each aniline studied. The various thermodynamic parameters as evaluated on the basis of these Arrhenius plots are recorded in Table 2.

A perusal of the data in Table 2 clearly indicates that these reactions are characterized by a low value for the energy of activation, E_a, and a large negative value for the entropy of activation, ΔS^{*}. The high negative value of ΔS^{*} suggests the formation of a charged and rigid transition state, which is expected to be strongly solvated. The low value of the energy of activation is of the order of the value for bimolecular reactions in solution. Since the reactions are of the ion–dipolar type [6–8], it is expected that the entropy of the activated complex for all these anilines should be nearly of the same order of magnitude. However, because of differences in the polarity of different anilines, the extent of solvation should be different and hence the experimental value of ΔS^{*} may be different for different anilines, as observed by us in the present studies. Further, the free energy of activation, ΔF^{*}, and the activation energy, E_a, in each case, is of a comparable order of magnitude, suggesting that the mechanism for all these anilines should be similar.

To test the validity of the isokinetic relationship [2] given by

$$\Delta H^{*} = \beta \Delta S^{*} \qquad (1)$$

a plot of ΔS^{*} vs. ΔH^{*} was made (Fig. 1): this plot was found to be linear (correlation coefficient being 0.97) showing that the isokinetic relationship is being followed. The value of the isokinetic temperature, β, was found to be 278 K. The validity of this relationship further suggested that the mechanism for all these oxidations should be similar.

Validity of LFER

The second-order rate coefficients (k_2) for different anilines along with various σ values, viz. σ for the Hammett equation [9], σ^0 for the Taft equation [10], σ^+ for the equation of Brown and Okamoto [11], σ^n for the equation of Van Bekkum et al. [12] and σ_p^0 for the equation of Sekigawa [13] (taken from the literature [1]) are recorded in Table 3.

TABLE 2

Thermodynamic parameters for different anilines

Substituent	E_a (kcal mole^{-1})	ΔF^{+} (kcal mole^{-1})	$-\Delta S^{+}$ (e.u.)	ΔH^{+} (kcal mole^{-1})
–H	6.85	20.88	47.92	6.24
p-Cl	10.43	21.02	36.68	9.81
p-OC_2H_5	8.32	18.80	36.30	7.70
p-OCH_3	7.05	18.95	40.93	6.44
p-CH_3	3.75	20.57	57.04	3.14
o-OCH_3	2.19	20.33	61.39	1.57

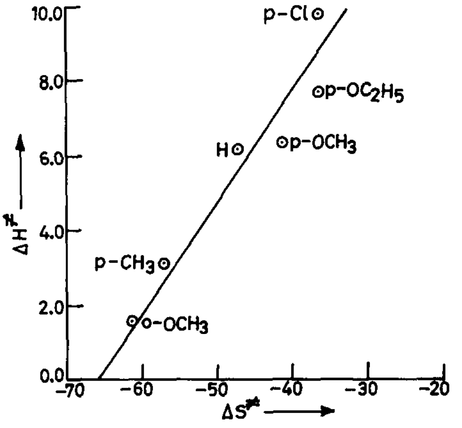


Fig. 1. Isokinetic relationship.

To test the validity of the different LFERs, plots were made for the Hammett equation (Fig. 2), Taft equation (Fig. 3), Van Bekkum equation (Fig. 4), Sekigawa equation (Fig. 5) and for the Brown and Okamoto equation (Fig. 6). An examination of these curves will show that, except for the Brown and Okamoto plot, all other plots are non-linear. The linearity of plot between log k^1/k^1_H and σ^+ (correlation coefficient 0.98 and slope $\rho = -1.67$) for the Brown and Okamoto plot indicates the validity of the linear free energy relationship as proposed by them [11], for these reactions. The concave upwards Hammett plot indicates that the electron-donating groups stabilize, by resonance, a transition state having a high positive charge on the reaction centre which in these studies is obviously the nitrogen of the NH_2 group. This facilitates the bond-breaking process in the transition state. However, if the curvature obtained in this plot is due to resonance in the transition state, the lower rates should be obtained with the *meta* substituents which cannot interact with the reaction site in the transition state [14]. This was observed by us in a separate study: the reactions in the case of oxidation of *m*-toluidine, *m*-chloroaniline, *m*-nitroaniline, *m*-

TABLE 3

Values for different parameters for different LFERs at 25°C

Substituent	$k_2 \times 10^3$	k^1_2/k^1_2H	σ	σ^0	σ^+	σ^n	σ^0_p
−H	5.6	1.0	0	0	0	0	0
p-Cl	3.7	0.66	0.23	0.27	0.114	0.373	0.243
p-OCH_3	138.8	24.99	−0.27	−0.12	−0.778	−0.111	−0.285
p-CH_3	10.7	1.92	−0.17	−0.15	−0.311	−0.129	−0.10
p-OC_2H_5	155.5	28.0	−0.25				
o-OCH_3	16.6						

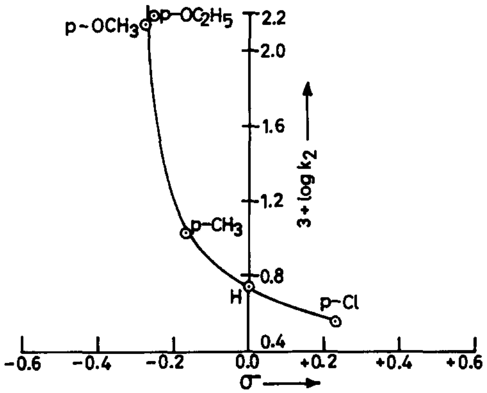


Fig. 2. Correlation with σ (Hammett) for various substituents.

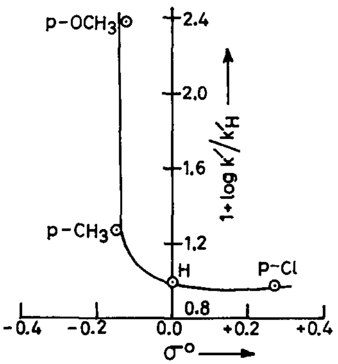


Fig. 3. Correlation with σ^0 (Taft) for various substituents.

methoxyaniline and *m*-ethoxyaniline were so slow that they could not be studied with reasonable accuracy under similar conditions for comparison. On the basis of the foregoing discussion, it can be concluded that the

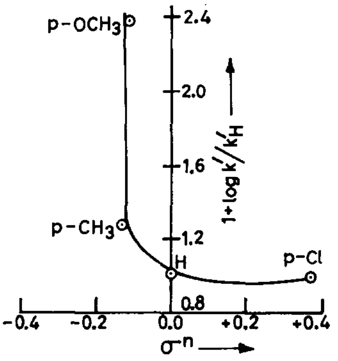


Fig. 4. Correlation with σ^n (Van Bekkum) for various substituents.

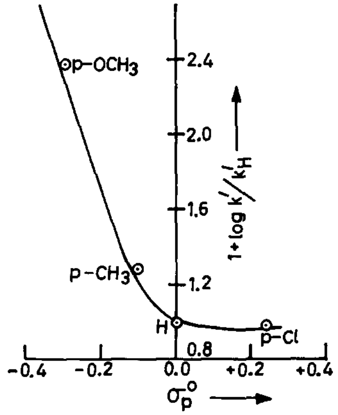


Fig. 5. Correlation with σ_p^0 (calculated by Sekigawa) for various substituents.

transition state, in these cases, is formed with a high positive charge on the nitrogen of the NH_2 group.

The linear Brown and Okamoto plot (Fig. 6) further confirms that the transition state formed should have a considerable positive charge. The value of the reaction constant, ρ, was found to be -1.67, which suggested that the electron-withdrawing groups in the nucleus retarded the reaction while electron-donating groups accelerated it and an electrophilic attack of the periodate (IO_4^-) anion on the $-NH_2$ nitrogen occurs in the rate-determining step. Non-linear Taft (Fig. 3) and Van Bekkum (Fig. 4) plots suggested the involvement of resonance interaction in these oxidation reactions. Similarly, the non-linear Sekigawa plot (Fig. 5) indicated that the ionisation of the

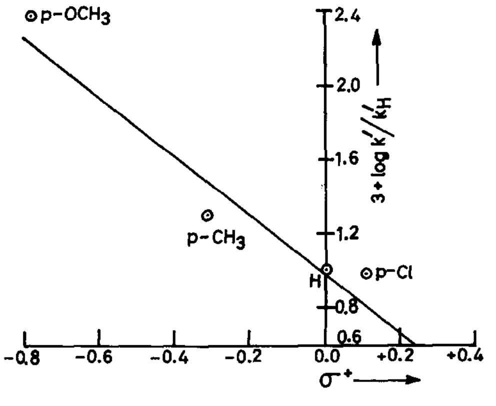
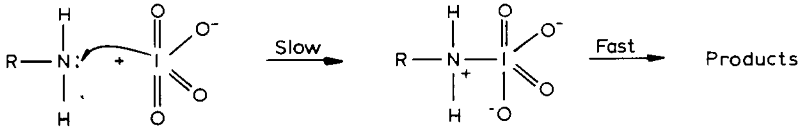


Fig. 6. Correlation with σ^+ (Brown and Okamoto) for various substituents.

anilines is not a deciding step in the reaction mechanism.

On the basis of the foregoing studies, the following scheme is proposed for the general attack by the periodate ion on anilines in the rate-determining step. However, further steps leading to the formation of product, may be different for different substituents present in the aniline nucleus, depending on the nature of the substituents and products formed.



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