

## Periodate Oxidation of Aromatic Amines: Studies on the Role of Substituents and Linear Free Energy Relationships

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The effect of substituents on the periodate oxidation of anilines has been studied in acetone-water medium. The validity of various linear free energy relationships has been tested and an attempt has been made to correlate the findings with the expected mechanism for this reaction series. Some of the results have been found to differ from the earlier works.

### INTRODUCTION

The Hammett equation and its modified forms<sup>1</sup>, all known as linear free energy relationships LFERs are based on the generalization that the reactions of a particular reaction series follow a similar mechanism and so LFERs have been found useful for correlating the reaction rates and equilibrium constants for *meta*- and *para*-substituted benzene derivatives. Srivastava *et al.*<sup>2</sup> studied the LFERs for the periodate oxidation of five anilines in 15% acetone-water medium taking the anilines in excess and reported the nonlinear Hammett relationship for this reaction series. Rao *et al.*<sup>3</sup> reported a linear Hammett relationship for this reaction series.

It is clear that the reported studies are contradictory and the periodate oxidation of more anilines should be undertaken to get a more clear picture. Further, it also appears worthwhile to make studies by taking the oxidant in excess. Therefore, we have tested the validity of Hammett and other LFERs for this reaction series by studying the periodate oxidation of eight anilines in 10% (v/v) acetone-water medium and taking the periodate in excess. Further, a few *meta*-substituted anilines have also been subjected to investigation to support a few observations. Some of the results have been found to differ from the earlier reported work.

### EXPERIMENTAL

Sodium meta-periodate and anilines used were of Loba G.R. grade or E. Merck grade. These were used after crystallization or redistillation in presence of zinc dust. All other chemicals used were of A.R. grade. Doubly distilled water was used for preparation of solutions and reaction mixtures.

The reactions being quite fast at ordinary temperatures were studied in 10% acetone-water medium and in absence of any catalyst.

Because of the formation of coloured products, the progress of the reactions was followed by recording the absorbance at different  $\lambda_{\max}$  (Table-1) of the reaction mixture at different intervals of time on Shimadzu double beam spectrophotometer, UV-150-02. Studies were confined to the early stage for which the  $\lambda_{\max}$  in each case did not change.

TABLE-1  
 $\lambda_{\max}$  OF REACTION MIXTURES FOR THE PERIODATE  
OXIDATION OF VARIOUS SUBSTITUTED ANILINES

Aniline	$\lambda_{\max}$ (nm)
Aniline	355-360
<i>p</i> -ethylaniline	480
<i>p</i> -chloroaniline	430
<i>p</i> -bromoaniline	450
<i>p</i> -methylaniline	470
<i>m</i> -methylaniline	540
<i>p</i> -methoxyaniline	475
<i>p</i> -ethoxyaniline	485

## 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 method<sup>4</sup> was employed for evaluating the pseudo first order rate constants. The pseudo first order rate

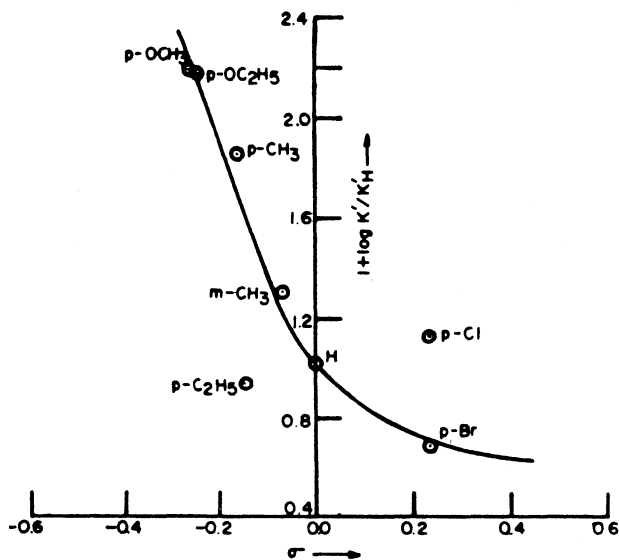


Fig. 1. Correlation with  $\sigma$  (Hammett) for various substituents

constants were divided by the concentration of periodate to get the second order rate constants ( $k_2$ ). It is important to mention here that initial rates have been used by Srivastava *et al.*<sup>2</sup> for testing the validity of LFERs and that it is always better to use rate constants for such studies as done by Rao *et al.*<sup>3</sup>

The second order rate constants ( $k_2$ ) for different anilines alongwith the various substituent constant values *viz.*  $\sigma$  for Hammett equation<sup>1</sup>,  $\sigma^0$  for Taft equation<sup>5</sup>,  $\sigma^+$  for the equation of Brown and Okamoto<sup>6</sup>,  $\sigma^n$  for the equation of Van Bekkum *et al.*<sup>7</sup> and  $\sigma_p^0$  for the equation of Sekigawa<sup>8</sup> are recorded in Table-2.

TABLE-2  
SECOND ORDER RATE CONSTANTS AND SUBSTITUENT  
CONSTANTS FOR DIFFERENT ANILINES

Substituent	$k_2 \times 10^2$ lit mol <sup>-1</sup> sec <sup>-1</sup>	$k_2/k_H$	$\sigma$	$\sigma^0$	$\sigma^+$	$\sigma^n$	$\sigma_p^0$
-H	1.45	1.00	0.00	0.00	0.00	0.00	0.00
<i>p</i> -C <sub>2</sub> H <sub>5</sub>	1.24	0.86	-0.15	—	—	—	—
<i>p</i> -Cl	2.00	1.38	0.23	0.27	0.114	0.238	0.243
<i>p</i> -Br	0.70	0.48	0.23	0.26	0.150	0.265	0.244
<i>p</i> -CH <sub>3</sub>	13.8	9.51	-0.17	-0.15	-0.311	-0.129	-0.100
<i>m</i> -CH <sub>3</sub>	2.88	1.98	-0.07	-0.07	—	-0.07	—
<i>p</i> -OCH <sub>3</sub>	23.0	15.86	-0.27	-0.12	-0.78	-0.111	-0.285
<i>p</i> -OC <sub>2</sub> H <sub>5</sub>	22.2	15.31	-0.25	—	—	—	—

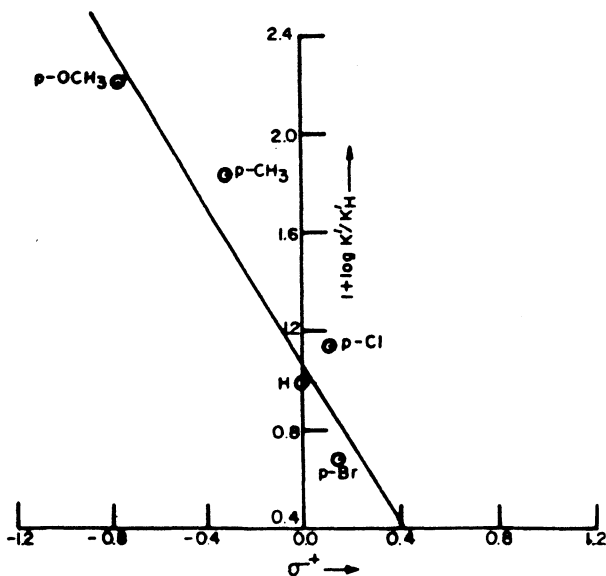


Fig. 2. Correlation with  $\sigma^+$  (Brown and Okamoto) for various substituents

The graphical plots observed for Hammett equation, Taft equation, Van Bekkum equation, Sekigawa equation and Brown and Okamoto equation are given in Figs. 1 to 5 respectively. An examination of Hammett plot shows that no linearity is obtained and the curve on the other hand is concave upwards. This is contradictory to the earlier reported work<sup>3</sup>. Such a concave upward plot indicates that the electron donating substituents stabilize by resonance<sup>169</sup>, a transition state having a high positive charge on the reaction centre<sup>9</sup> which in this case obviously is the nitrogen of the anilino group. This facilitates the bond breaking process in the transition state. On the other hand an electron withdrawing substituent increases the capacity of the anilino nitrogen for a more negative charge in the transition state relative to the positive charge on the same nitrogen in the ground state. This facilitates the bond making process in the transition state. If the type of curvature observed in Fig. 1 is due to resonance in the transition state, the lower rates should be obtained with the *meta* substituents since it is these substituents which cannot interact through resonance with the reaction site in the transition state. It was found by us that the oxidation of many *meta* substituted derivatives of aniline *viz.* *m*-chloroaniline, *m*-bromoaniline, *m*-nitroaniline, *m*-methoxyaniline and *m*-ethoxyaniline is so much slow that it could not be studied with reasonable accuracy under similar conditions for comparison. However the only exception found was *m*-toluidine but an examination of the data reveals that the rate is much lesser in this case in comparison to that observed for the oxidation of *p*-toluidine. Thus, it can be concluded that the transition state is formed in this reaction with a high positive charge on the nitrogen of the anilino group.

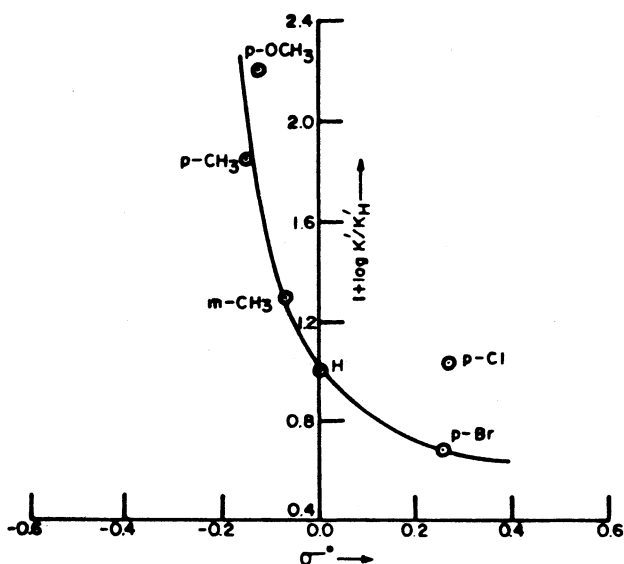


Fig. 3. Correlation with  $\sigma^0$  (Taft) for various substituents

The Taft plot (Fig. 3) and Van Bekkum plot (Fig. 4) are both nonlinear suggesting thereby the involvement of resonance interaction in the oxidation of anilines under consideration<sup>5,7</sup>. Similarly the nonlinear Sekigawa plot (Fig. 5) indicates that the ionisation of the anilines is not a deciding step in the reaction mechanism.<sup>8,9</sup>

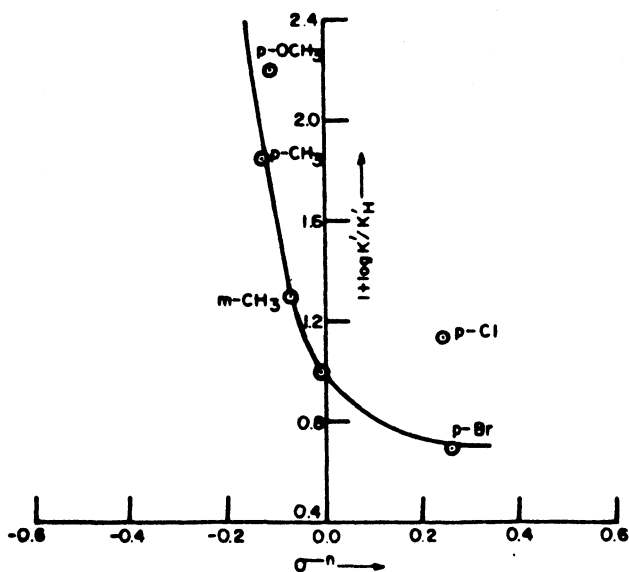


Fig. 4. Correlation with  $\sigma^n$  (Van Bekkum) for various substituents

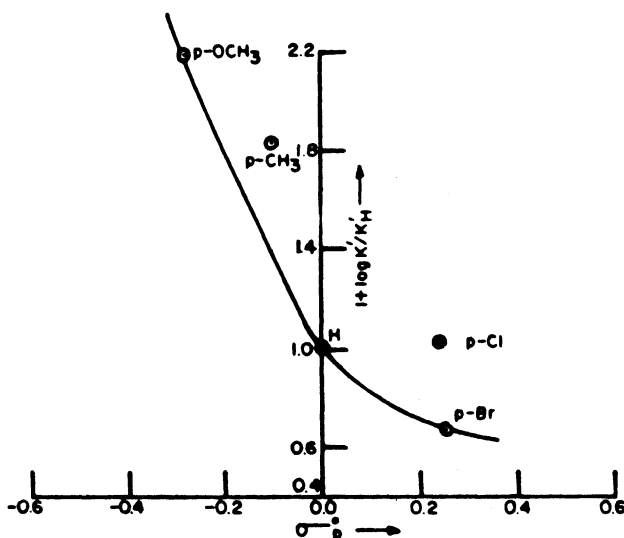
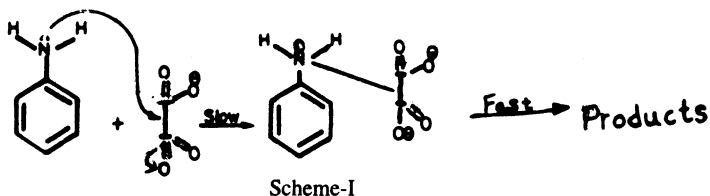


Fig. 5. Correlation with  $\sigma^0_p$  (Sekigawa) for various substituents

An examination of the linear Brown and Okamoto plot (Fig. 2) reveals that the transition state formed should be with a considerable positive charge<sup>9</sup>. Least square method was applied for evaluating the value of  $\rho$  of the reaction constant  $\rho$  which came out to be  $-1.54$ . The negative value of  $\rho$  suggests that the electron withdrawing groups in the nucleus retard the reaction while the electron donating groups accelerate it and an electrophilic attack by the periodate ion on the anilino nitrogen occurs for this oxidation process. A negative value of  $\rho$  for the Brown and Okamoto plot indicates the stabilization of positive charge on the transition state<sup>10</sup>.

Since these reactions are of ion-dipolar type<sup>2, 3, 11-13</sup> and a linear Brown and Okamoto plot suggests that the reaction series should follow a similar mechanism and our observation suggests that the order is one in each reactant, the following initial step may be proposed for the general attack of periodate ion on the anilines (Scheme-I).



Further steps leading to the formation of final products may depend on the different substituents present in the aniline nucleus.

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