

Effect of multiple substituents on oxidation of phenyl styryl ketone and its substituted analogues by V(V) in acid medium: A kinetic study

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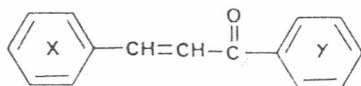
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Kinetics of oxidation of phenyl styryl ketone (PSK) and its substituted analogues by V(V) has been investigated in 80% aqueous acetic acid and 2M H₂SO₄ medium in the temperature range 303-328K. The products have been identified as benzoic acid and phenylacetaldehyde under kinetic conditions and stoichiometry is 2:1 [V(V):PSK]. The rates are enhanced by electron releasing substituents in both the phenyl rings and decreased by electron withdrawing substituents. The mechanism proposed envisages attack by V(V) molecule on >C=O group. Linear Hammett's plots are obtained for various substituents in benzaldehyde moiety of PSK for every substituent in acetophenone moiety and vice versa. From this the applicability of interactive free energy relationship has been tested. The cross interaction constants q_x and q_y are 0.550 and 0.690 at 323K.

During the oxidation of phenyl styryl ketone (PSK) and its substituted analogues by different oxidants¹⁻¹¹, the products reported were different depending on the nature of the oxidant and other conditions. For example, in Cr(VI) oxidation¹ of PSK, >C=C< was reported as the site of attack and the reaction was assumed to proceed via formation of a π complex with the oxidant. With potassium superoxide², however, the lone pair electrons of carbonyl oxygen were shown to be involved in the oxidation. A symmetric electrophilic attack on the carbon-carbon double bond, leading to the formation of a partially bridged activated complex, which later gives the product epoxide, has been proposed during the oxidation of PSK by pyridinium chlorochromate³.

PSK is structurally an interesting compound due to the presence of >C=C< and >C=O between two phenyl rings where ring X comes from benzaldehyde moiety and ring Y comes from acetophenone moiety (Structure 1). The present work on the oxidation of phenyl styryl ketone and its substituted analogues by V(V) is aimed at finding



(1)

out how the rate changes with the substituents when the substituents are changed simultaneously in both the rings and to analyse multiple substituent effects quantitatively, if possible, by applying the interactive free energy relationship.

Materials and Methods

PSKs were prepared¹² by Claisen Schmidt condensation of corresponding substituted benzaldehydes and acetophenones in the presence of aq. NaOH and ethanol, and purified by column chromatography. Ammonium meta vanadate used was of AR Merck grade. Pure acetic acid free from oxidisable impurities was obtained by refluxing acetic acid with chromium trioxide for 6 hr and distilling it twice. The rate of the reaction was followed by measuring the disappearance of V(V) by adding aliquots of the reaction mixture to known excess of Fe(II) and estimating the unreacted Fe(II) against standard V(V) using barium diphenyl amino sulphonate as indicator. In most of the experiments the ratio of [substrate] to [V(V)] was kept at 10:1. The reactions were carried out in 80% (v/v) acetic acid-H₂O mixtures.

Stoichiometry and product analysis

Stoichiometric runs with [V(V)] \gg [PSK]

revealed that one mole of PSK requires four moles of V(V). The products of oxidation were identified as benzoic acid and phenyl acetic acid. Both were identified by TLC and ^1H NMR spectra. Under kinetic condition (i.e., pseudo-first order condition i.e., $[\text{PSK}] \gg [\text{V(V)}]$) one mole of PSK required two moles of V(V). The products of oxidation were identified as benzoic acid and phenylacetaldehyde. Benzoic acid was identified by its methyl ester through TLC. Phenylacetaldehyde was identified by spot test analysis¹³ and TLC as well.

Results and Discussion

Experiments were carried out under pseudo-first order conditions with $[\text{PSK}] \gg [\text{V(V)}]$. The order with respect of $[\text{V(V)}]$ was found to be unity as seen from the linear plots of $\log(a/a-x)$ vs time (Figure 1A). It was observed that as the concentration of V(V) increased, the rate of reaction decreased to a certain extent probably due to the presence of different V(V) species¹⁴ in solution such as, VO_2^+ , VO_2^{2+} , V(OH)_3^{2+} , etc. The order with respect to $[\text{PSK}]$ was found to be less than one (~ 0.8) in all the cases as revealed by slope of the linear plot of $\log k'_{\text{obs}}$ vs $\log [\text{PSK}]$ in the concentration range of $[\text{PSK}] = 5-12.5 \times 10^{-2}$ mol dm^{-3} (Figure 1B). The plot of $1/k'_{\text{obs}}$ vs $1/[\text{PSK}]$ was linear with an intercept on Y-axis (Figure 1C), indicating formation of 1:1 complex between PSK and V(V) prior to oxidation in a rate determining step.

The rate of oxidation enhanced with the increase in $[\text{H}_2\text{SO}_4]$ (Table I). On the basis of the effect of $[\text{H}^+]$ and several other investigations it was shown by earlier workers¹⁵⁻¹⁸ that the most probable reactive species of V(V) at higher acidities is V(OH)_3^{2+} as per the following equilibrium.



At higher concentrations of H_2SO_4 , $[\text{V(OH)}_3\text{HSO}_4]^+$, $[\text{V:O(OH)}_2\text{SO}_4]^+$ and $[\text{V(OH)}_3^{2+}(\text{SO}_4^{2-})]$ (H_3O^+) (H_2SO_4^-) have also been considered as probable reactive species. If V(OH)_3^{2+} is to be the reactive species the rate should increase with $[\text{H}^+]$ which infact was observed in the present study. This receives support from solvent effect studies also. The rate of oxidation increased with the increase in percentage of acetic acid or decrease in dielectric

Table I—Effect of H_2SO_4 on the reaction rate in V(V) oxidation of PSK

$\{[\text{PSK}] = 1.00 \times 10^{-2}$ mol dm^{-3} , $[\text{V(V)}] = 1.00 \times 10^{-3}$ mol dm^{-3} , $[\text{AcOH}] = 80\%$, Temp. = 323K}

H_2SO_4 (mol dm^{-3})	$k \times 10^3$ (min^{-1})
0.500	2.30
1.00	5.37
1.50	11.3
2.00	16.6

constant (D) of the medium. The plot of $\log k'_{\text{obs}}$ vs $1/D$ is linear with a positive slope indicating a reaction between positive ion $\{\text{V(OH)}_3^{2+}\}$ and dipole $\{\text{PSK}\}$ (Figure 1D).

Mechanism

The reaction between PSK and one electron oxidant like V(V) is expected to proceed via intermediate formation of free radicals. Presence of radicals was confirmed by formation of polymer when acrylonitrile (monomer) was added to V(V)-PSK redox system. In the absence of PSK no polymer formation was observed. The IR spectrum of the polymer showed a sharp peak at 1710 cm^{-1} indicating the presence of $\text{C}_6\text{H}_5\text{C}=\text{O}$ in the polymer chain.

It is now well established that oxidation of ketones by one electron metal ion oxidants attack the carbonyl group followed by the breakdown of either a C-C or a C-H bond. From the stoichiometry, product analysis, presence of free radicals and foregoing discussion, the mechanism of oxidation of PSK by V(V) could be written as shown in Chart I.

Assuming the decomposition of the intermediate complex as the rate determining step, one can obtain the rate law as,

$$\text{rate} = \frac{kK_1K_2[\text{PSK}][\text{VO}_2^+][\text{H}_3\text{O}^+]}{1 + K_2[\text{PSK}]}$$

$$-\frac{2.303d\log[\text{V(V)}]_t}{dt} = k'_{\text{obs}}$$

$$= \frac{kK_1K_2[\text{PSK}][\text{H}_3\text{O}^+]}{1 + K_2[\text{PSK}]}$$

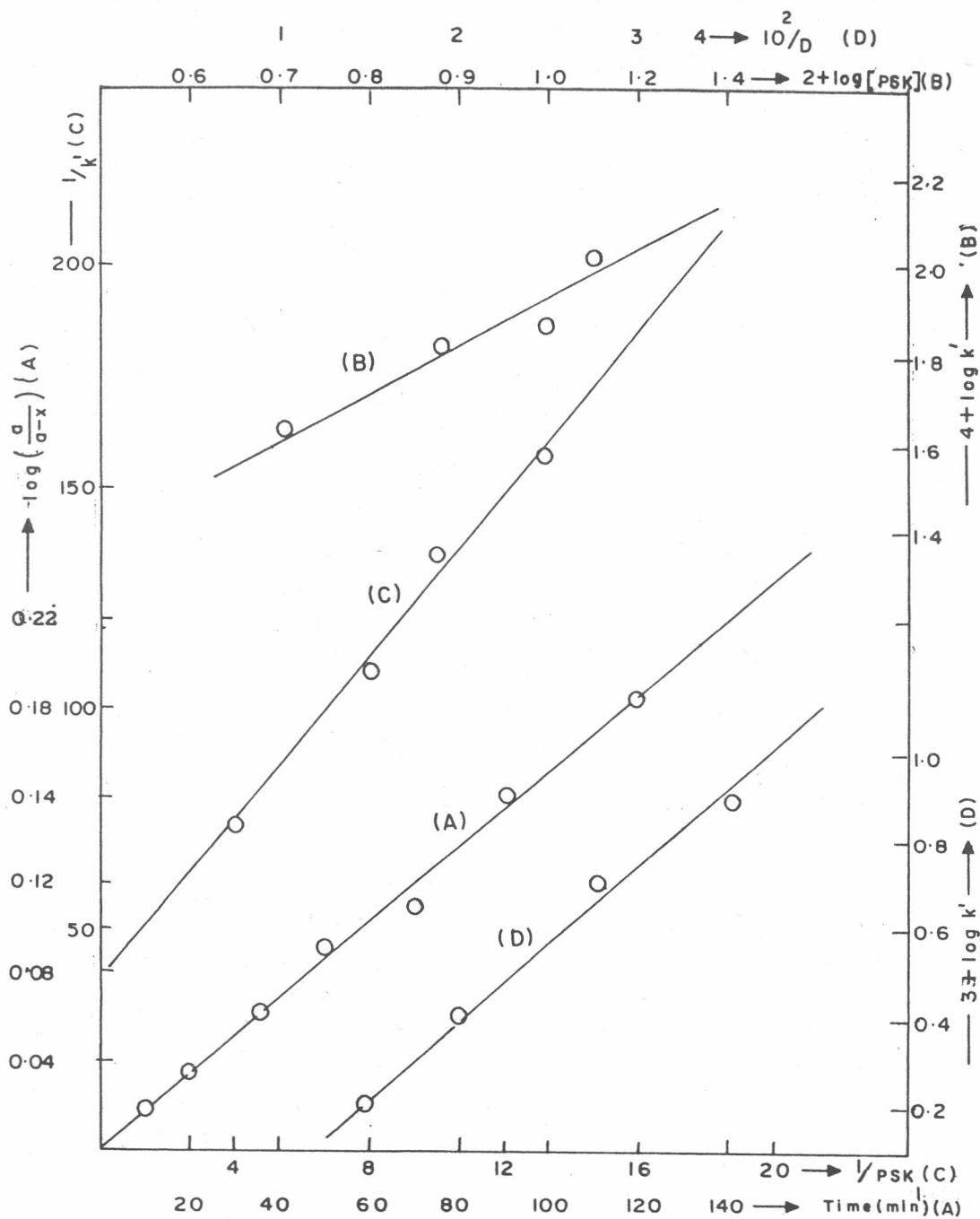


Figure 1A—Plot of $\log(a/a-x)$ vs time
 {[V(V)]=0.005 M; [PSK]=0.050 M;
 [H₂SO₄]=2.00 M; [AcOH]=70% (v/v);
 Temp=318K}

Figure 1B—Plot of $4 + \log k'_{\text{obs}}$ vs $2 + \log [\text{PSK}]$
 {[PSK]=5.00-12.5×10⁻² M; [V(V)]=0.004 M
 [H₂SO₄]=2.00 M; [AcOH]=70% (v/v);
 Temp=317K}

Figure 1C—Plot of $1/k'_{\text{obs}}$ vs $1/[\text{PSK}]$

Figure 1D—Plot of $3 + \log k'_{\text{obs}}$ vs $10^2/D$

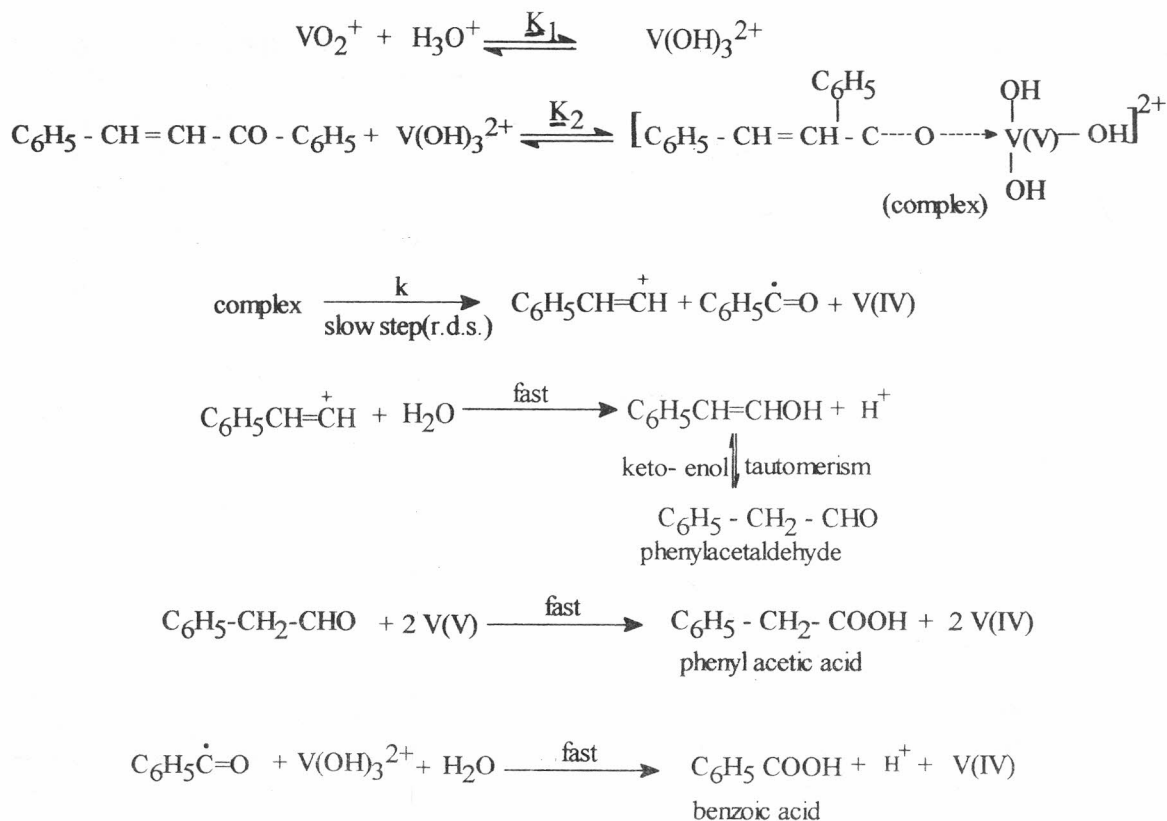


Chart 1

where k'_{obs} is the observed pseudo first order rate constant. The equation may be rewritten as,

$$\frac{1}{k'_{\text{obs}}} = \frac{1}{kK_1K_2[\text{PSK}][\text{H}_3\text{O}^+]} + \frac{1}{kK_1[\text{H}_3\text{O}^+]}$$

At constant $[\text{H}_3\text{O}^+]$, a plot of $1/k'_{\text{obs}}$ vs $1/[\text{PSK}]$ is expected to give a straight line with an intercept which in fact has been observed in the present investigation, supporting the proposed mechanism.

The effect of substituents on the reaction rate was studied by varying the substituents in both the rings (X and Y). The order of reactivity with various substituents in benzaldehyde ring for any particular substituent in acetophenone moiety is $p\text{-CH}_3 > \text{H} > p\text{-Cl} > m\text{-Cl} > p\text{-NO}_2$. The order of reactivity of various substituents in acetophenone ring for any substituent in benzaldehyde moiety is $p\text{-CH}_3 > \text{H} > p\text{-Cl} > p\text{-NO}_2$. This indicates that the rate is accelerated by electron releasing substituents while electron withdrawing substituents retard the reaction.

The mechanism envisaged for the V(V) oxidation of PSKs involves an electrophilic attack on carbonyl oxygen in a single concerted step resulting in reductive complex formation between

$>\text{C}=\text{O}$ and V(V). This receives support from the study of the effect of substituents in both the rings. For example, the observed rate constant (k') for simple PSK at 313K is 3.84×10^{-3} litre mol^{-1} sec^{-1} . When methyl group is introduced in the *para*-position of ring Y with H in ring X the rate constant increased to 6.26×10^{-3} litre mol^{-1} sec^{-1} . When methyl group is introduced in ring X at *para*-position instead, the rate increased to 57.6×10^{-3} litre mol^{-1} sec^{-1} . When methyl groups are introduced in the *para*-position in both the rings the rate increased further to 71.5×10^{-3} litre mol^{-1} sec^{-1} . It is therefore clear, that introduction of an electron releasing group increases the rate and the increase is more pronounced when it is present in ring X than in ring Y. *p*-Me substituent in ring X shows higher reactivity probably because of positive hyperconjugative effect, which dominates due to extended conjugation of phenyl ring with $>\text{C}=\text{C}<$ thus favouring a pronounced electrophilic attack on $>\text{C}=\text{O}$ group, compared to *p*-Me in ring Y.

With *p*-NO₂ substituent in ring X the rate constant decreased ($k' = 3.14 \times 10^{-3}$ litre mol^{-1} sec^{-1}) probably due to -M effect. However, when nitro

group is present in *para*-position in ring Y, the rate constant increased compared to simple PSK. The reason for this could be due to -M effect of *p*-NO₂ resulting in development of partial positive charge at the carbonyl carbon and this in turn helps in drawing electrons from the styryl group to make the carbonyl carbon more electron rich. This probably facilitates the electron transfer from carbonyl oxygen to metal ion.

With electronegative atoms like chlorine present in *para*-position, the rate of oxidation retarded compared to simple PSK. The retarding effect was more pronounced when the group was in ring Y, probably due to -I effect of the group. The rate of oxidation of *p*-Cl group in ring X is almost same (Table II) as that of simple PSK which could be due to -I effect getting neutralised by +M effect, as well as the effect of extended conjugation.

Applicability of Hammett's equation

The Hammett's reaction constant ρ_x values have been calculated from the slope of the linear plot of

$\log k''$ vs σ (Figure 2A) for a given substituent in ring Y. They are for *p*-CH₃ (-0.500); H (-0.250) and *p*-Cl (-0.150). The ρ_x values obtained with various substituents in ring X were found to be different for different substituents in ring Y. Similarly the values of ρ_y for a given substituent in ring X are *p*-CH₃ (-0.675); H (-0.600); *p*-Cl (-0.500); *m*-Cl (-0.275); *p*-NO₂ (-0.175). The negative values obtained in all the cases indicate formation of an electron deficient transition state as expected for an electron transfer reaction. It is clear from the values of $\rho_{X(Y)}$ or $\rho_{Y(X)}$ that the magnitude of ρ for various substituents in any particular ring is a function of the nature of substituent present in the other ring.

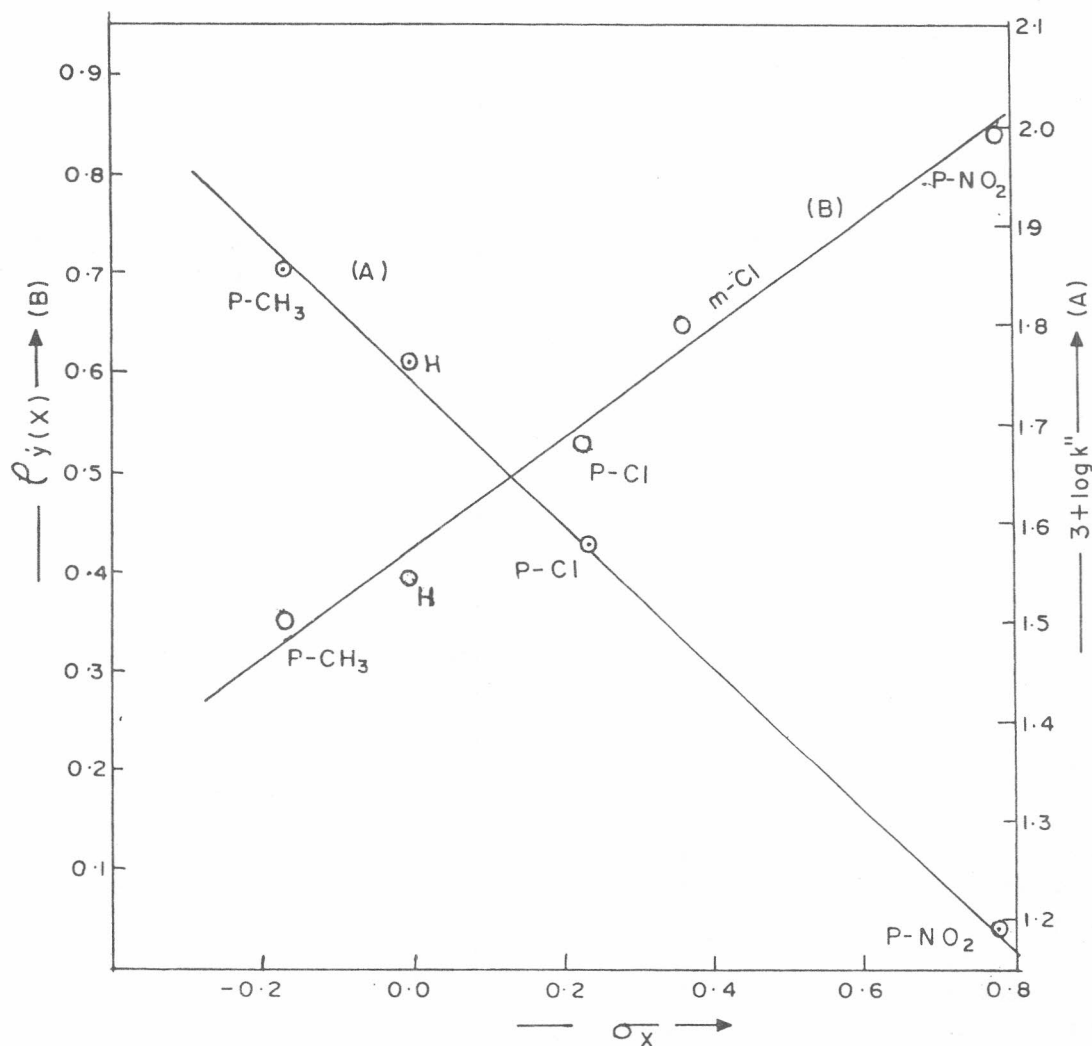
The results were analysed in terms of interactive free energy relationships for multiple substituent effects as discussed by Ruasse *et al.*^{19,20} during their work on bromination of stilbenes. The most probable site of attack suggested there was >C=C< which is between the two phenyl rings. For this

Table II—Bimolecular rate constants for oxidation of PSK by V(V)

{[PSK]=1.00×10⁻² mol dm⁻³, [V(V)]=1.00×10⁻³ mol dm⁻³, [H₂SO₄]=2.00 M, [AcOH]=80% (v/v)}

Substitution in benzaldehyde ring X	Substitution in acetophenone ring Y	$k'' \times 10^3$ (lit mol ⁻¹ sec ⁻¹)			
		313	318	323	328K
	<i>p</i> -CH ₃	71.5	115	148	209
	H	57.6	80.8	122	189
<i>p</i> -CH ₃	<i>p</i> -Cl	37.7 ^(0.999)	70.3 ^(0.991)	72.3 ^(0.995)	125 ^(0.995)
	<i>p</i> -NO ₂	15.4	29.7	33.7	55.8
	<i>p</i> -CH ₃	6.26	8.33	13.7	16.5
	H	3.84	5.76	9.60	13.0
H	<i>p</i> -Cl	2.94 ^(0.967)	4.74 ^(0.965)	6.41 ^(0.998)	12.6 ^(0.860)
	<i>p</i> -NO ₂	42.3	75.2	94.2	152
	<i>p</i> -CH ₃	6.09	8.08	12.7	19.2
	H	4.16	5.58	8.55	12.3
<i>p</i> -Cl	<i>p</i> -Cl	3.46 ^(0.985)	4.14 ^(0.982)	6.21 ^(0.982)	9.44 ^(0.969)
	<i>p</i> -NO ₂	1.97	2.50	3.66	5.89
	<i>p</i> -CH ₃	3.46	4.32	6.91	10.6
<i>p</i> -NO ₂	H	3.14 ^(0.995)	4.29 ^(0.922)	6.66 ^(0.956)	9.42 ^(0.995)
	<i>p</i> -Cl	2.72	3.72	5.50	8.34
	<i>p</i> -CH ₃	4.16	5.88	8.17	12.3
<i>m</i> -Cl	<i>p</i> -Cl	3.12 ^(0.995)	4.11 ^(0.999)	6.83 ^(0.975)	10.8 ^(0.976)
	<i>p</i> -NO ₂	1.78	2.35	3.56	6.61

*In brackets are the correlation coefficients of Hammett's plots

Figure 2A—Plot of $3 + \log k''$ vs σ Figure 2B—Plot of $\rho_{Y(X)}$ vs σ_x

type of reaction the following equation was found to be applicable.

$$\frac{\rho_{Y(X)} - \rho_{Y(X_0)}}{\sigma_x} = \frac{\rho_{X(Y)} - \rho_{X(Y_0)}}{\sigma_y} = q$$

where $\rho_{X(Y_0)}$ and $\rho_{Y(X_0)}$ are reaction constants for various substituents in the rings X and Y respectively with H in the other ring. Similarly $\rho_{X(Y)}$ and $\rho_{Y(X)}$ are reaction constants for various substituents in rings X and Y respectively for a particular substituent in the other ring. σ_x and σ_y are the substituent constants of substituents in rings X and Y respectively. This equation must be true whatever the nature of the substituent in rings X or Y i.e., q (which is called the cross interaction constant) is expected to be same. In the case of

oxidation of aromatic anils by acid bromate²¹, where the site of attack is $>C=N-$, q_x and q_y are expected to be same. Infact the values reported ($q_x=0.750$ and $q_y=0.700$) are almost same suggesting that the site of attack is indeed $>C=N-$. Similarly in case of Os(VIII) catalysed oxidation of PSKs by IO_4^- (ref. 6) the cross interaction constants obtained were $q_x=0.41$ and $q_y=0.36$ which are almost similar. Here also the site of attack suggested was $>C=C<$. But in the present work where the site of attack is considered as $>C=O$, q_x (Figure 2B) and q_y were found to be 0.550 and 0.690 respectively at 323K. It is reported earlier during the oxidation of PSKs by Ce(IV)⁵ that q_x and q_y values differ considerably. In the present work although the q_x and q_y values are not

Table III—Values of q_x and q_y at different temperatures

Temperature (K)	q_x	q_y
313	0.600	0.700
323	0.550	0.690
328	0.500	0.650

Table IV—Comparison of q_x and q_y values in different reactions

Kinetic reaction	Site of attack	q_x	q_y
Oxidation of Anils by acid bromate ²¹	>C=N- in Anils	0.750	0.700
Os(VIII) catalysed oxidation of PSK's by periodate ⁶	>C=C< of PSK	0.410	0.360
Oxidation of PSK's by Ce(IV) ⁵	>C=O of PSK	-1.60	-0.800
Os(VIII) catalysed oxidation of PSK's by acid bromate	>C=C< of PSK	0.917	1.02
Oxidation of PSK's by V(V)*	>C=O of PSK	0.550	0.690

*Present work

significantly different, the values obtained at various temperatures (Table III) clearly indicate the trend which is unmistakable. To say that the q_x and q_y values (Table IV) can really throw light on the site of attack and/or capable of distinguishing one and two electron oxidants, more work has to be done with different one and two electron oxidants in different media to confirm the above conclusions. The work on this line is in progress.

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