# Study of Interactive Free-Energy Relationships on Ruthenium(III) Catalyzed Oxidation of Phenyl Styryl Ketone and Its Substituted Analogues by V(V) in Acid Medium

S. R. ANNAPOORNA, M. PRASAD RAO, B. SETHURAM

*Department of Chemistry, Osmania University, Hyderabad-500 007*

*Received 7 May 1999; accepted 18 April 2000*

ABSTRACT: Kinetics of Ru(III) catalyzed oxidation of phenyl styryl ketone (PSK) and its substituted analogues by V(V) has been investigated in aqueous acetic acid-sulphuric acid medium in the temperature range 298–313 K. First-order dependence each on [V(V)], [PSK], and [Ru(III)] was observed. Inverse first-order dependence was observed for [V(IV)]. The rate decreased with the increase in dielectric constant (*D*) of the medium. The rates were enhanced by electron-donating substituents in both the phenyl rings and decreased by electron-withdrawing substituents. Linear Hammett's plots were obtained for various substituents in benzaldehyde moiety of PSK for a given substituent in acetophenone moiety and vice versa. The mechanism proposed envisages formation of Ru(IV) from V(V) + Ru(III) reaction followed by the attack on $\rangle C{=}O$ by Ru(IV). Applicability of interactive free-energy relationship has been tested. The cross-interaction constants $q_x$ and $q_y$ have been determined at different temperatures and possible interpretations discussed. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 581–588, 2000

## INTRODUCTION

The usefulness of ruthenium(III) species as an oxidant in a variety of oxidative transformations [1] particularly in organic chemistry is now well recognized [2]. The expense of ruthenium metal provided incentive for the development of catalytic procedures. Ru(III) catalysis of several redox reactions involving various substrates has been reported [3,4]. We have recently reported the oxidation of phenyl styryl ketones (PSK) by V(V) in acid medium and proposed a radical mechanism [5]. Extensive study of the effect of substituents on rates of this reaction has shown the general applicability of interactive free-energy relationships. Com-

---

*Correspondence to:* B. Sethuram, Department of Chemistry, Osmania University, Hyderabad–500 007, India parison with earlier work [5] indicates that the cross-interaction constants $q_x$ and $q_y$ are not equal, supporting the proposed mechanism and suggesting $>C{=}O$ attack. Extending this line of thinking, we wanted to find out what type of results can be expected when Ru(III) is added to the system above and what information can be drawn from the substituent-effect studies of such a system. The main objectives of the present study are to find out (1) whether there is any Ru(III) catalysis and, if so, whether it results in a change in the mechanism from radical to ionic; (2) the nature of the radicals or ions formed; (3) the nature of the oxidizing species Ru(IV), Ru(V), etc.; (4) the effect of substituents on the rate of the reaction; and (5) whether cross-interaction constants ($q_X$ and $q_Y$) could be used for predicting the site of attack as well as the nature of the type of electron transfer, one or two; and (6) whether (a) Ru(III) is oxidized to Ru(IV), Ru(V), or Ru(VI); and (b) if so, which one of them is reduced by PSK to give what type of species, Ru(II) or Ru(III); and (c) which group, $>C{=}C<$ or $>C{=}O$, is attacked and all this with the help of $q_x$ and $q_y$ values.

## MATERIALS AND METHODS

Ru(III) chloride solution was prepared as per the standard procedure [6] using a Johnson-Mathey sample. Preparation [7,8], purification of PSKs, the details of titrimetric procedure used to follow the reaction, and product analysis procedures are given in our earlier paper [5]. Unless otherwise specified, all the experiments are conducted under the condition [substrate]:[V(V)] at a 10:1 ratio and in 80% (v/v) acetic acid–$H_2O$ mixtures as solvent. The spectral measurements were made on a Hitachi UV-Visible spectrophotometer model 3410. The HPLC system used for analysis of products includes Hitachi (E. Merck) equipment, $C_{18}$ column (25 cm) $\mu$ Bondapak, and UV-Visible detector. The column effluents were monitored at 210 nm, with a flow rate of 1.00 ml/min in a buffer system, which is $KH_2PO_4$ (0.065 M):acetonitrile (3:1).

## STOICHIOMETRY AND PRODUCT ANALYSIS

Stoichiometric runs with [V(V)] $\gg$ [PSK] revealed that one mole of PSK requires four moles of V(V) both in the absence and presence of Ru(III). The products of oxidation were identified as benzoic acid and phenyl acetic acid by HPLC, which were confirmed by comparing with authentic samples. The intermediate product, i.e., phenyl acetaldehyde, was identified by spot-test analysis [9].

## RESULTS AND DISCUSSION

Under the conditions [PSK] $\gg$ [V(V)], the order in [V(V)] was found to be unity as seen from the linear plot of $\log(a/a - X)$ vs. time. From the slopes of such plots the pseudo-first-order rate constants ($k_{obs}$) were calculated. The order in [PSK] was also unity in all the cases, as revealed by the slope of the linear plot of $\log k_{obs}$ vs. log[PSK] in the concentration range of [PSK] $= 5 \times 10^{-3}$ to $4 \times 10^{-2}$ M (Fig. 1(a)). The order with respect to [Ru(III)] was also unity, as can be seen from the slope of the linear plot $\log k_{obs}$ vs. log[Ru(III)] in the concentration range of [Ru(III)] $= 7 \times 10^{-8}$ to $7 \times 10^{-7}$ M (Fig. 1(c)). The plot of $1/k_{obs}$ vs. 1/[PSK] was linear passing through the origin, sug-

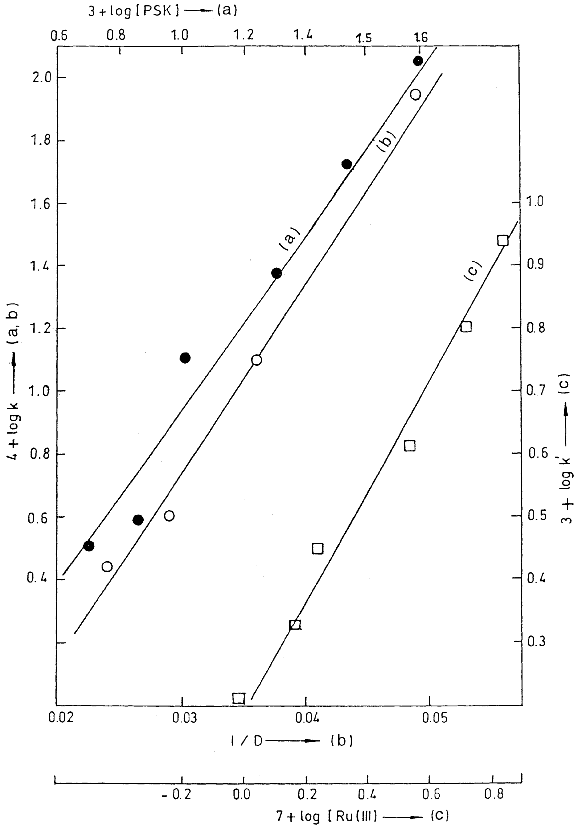


**Figure 1** Plots of (a): $\log k_{obs}$ vs. log[PSK]; (b): $\log k_{obs}$ vs. $1/D$; (c): $\log k_{obs}$ vs. log[Ru(III)].

gesting that no complex is formed between the oxidant and PSK, or the complex, if formed, is too weak and unstable to be deciphered from such plots. The rate of oxidation enhanced with the increase in $[H_2SO_4]$ in the range 0.500–2.00 M and the order in $[H^+]$ was found to be unity. On the basis of the effect of $[H^+]$ and several other investigations, it was shown by earlier workers [10–13] that the most probable V(V) species at high acidities is $V(OH)_3^{2+}$ as per the following equilibrium:

$$VO_2^+ + H_3O^+ \longleftrightarrow V(OH)_3^{2+}$$

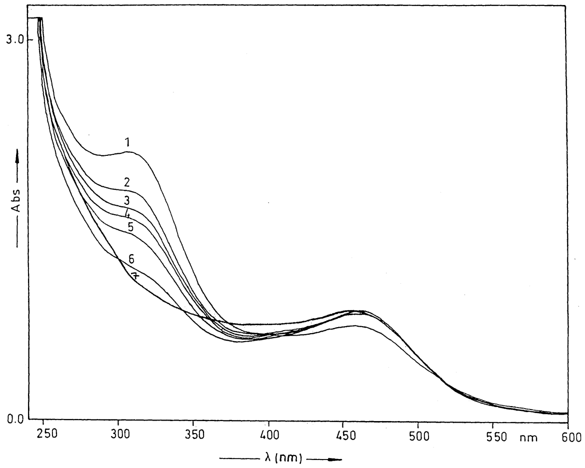


**Figure 2** λ(nm) vs. Abs. UV-visible absorption spectra of the reaction mixture containing Ru(III) + V(V) + PSK.

On addition of V(IV), the rate of the reaction decreased, showing retardation effect. The order in [V(IV)] was studied in the concentration range $1.00–10.0 \times 10^{-3}$ mol dm$^{-3}$ and was found to be inverse first order, and the rate constant changed from $2.05 \times 10^{-3}–3.31 \times 10^{-4}$ min$^{-1}$ in that range for five different concentrations. The other point of interest is to determine the nature of reactive species of Ru(III) chloride. Ruthenium(III) chloride exists in various forms in dilute HCl medium. Electronic spectral studies of Cady and Connick [14] and Connick and Fine [6] reveal that species such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$, $[RuCl(H_2O)_5]^{2+}$, and $[Ru(H_2O)_6]^{3+}$ are possible. Of all these species only $[Ru(H_2O)_6]^{3+}$ is present in larger proportion and is probably the most reactive species [15]. When Ru(III) is added to V(V), it is possible for Ru(III) to get oxidized to Ru(IV), Ru(V), or Ru(VI). Since Ru(V) and Ru(VI) are unstable in acid medium, one can expect that Ru(III) is oxidized only to Ru(IV). This was confirmed from spectral analysis from Ru(III) + V(V) solutions: A clear peak at 456 nm to a plateau extending from 430 to 490 nm similar to the one for Ru(IV) in $HClO_4$ reported by Wehner et al. [16] has been observed, and the peak of Ru(III) disappeared completely (Fig. 2, Scan. 7). When PSK was added to Ru(III)-V(V) mixtures, the PSK peak was reduced, while the peak at 456 nm corresponding to Ru(IV) remained constant as the time progressed (Fig. 2, Scan. 1–6), suggesting that V(V) reacts with Ru(III) in a fast step to give Ru(IV), which later oxidizes PSK in a slow step. At this point it is necessary to know whether Ru(IV) is oxidizing PSK by one or two electron-transfer mechanisms. If Ru(IV) gets reduced to Ru(II), the characteristic peak of the latter should have been observed at 530 nm. Since no such peak was observed, it is possible that Ru(IV) is oxidizing PSK by a one-electron transfer mechanism, resulting in the formation of Ru(III) and some radical from PSK. Since $[Ru(III)] \ll [V(V)]$, one should expect the Ru(III) thus formed in the preceding process to get immediately oxidized to Ru(IV), so that the concentration of Ru(IV) remained constant over a period of time. This has been observed in the present study, supporting our contention. One-electron transfer reagents generally attack $>C=O$ in preference to $>C=C<$ [20]. If Ru(IV) is assumed to attack $>C=O$ like other one-electron transfer reagents (viz., V(V), Ce(IV), Mn(III), etc.), it can result in the formation of benzoyl radical, as shown in mechanism (Scheme I).

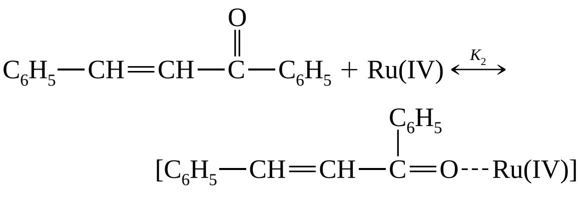
The rate of oxidation increased with the increase in percentage of acetic acid or the decrease in dielectric constant ($D$) of the medium. The plot of log $k_{obs}$ vs. $1/D$ was linear (Fig. 1(b)) with a positive slope indicating the reaction between a positive ionic species of Ru(IV) and a dipole PSK.

The reaction between PSK and the one-electron oxidant is expected to proceed via intermediate formation of free radicals. Presence of radicals was confirmed by the formation of polymer when acrylonitrile (monomer) was added to the {Ru(III) + V(V)} + PSK redox system. The presence of $C_6H_5C^{\bullet}=O$ was confirmed by the IR spectral peak at 1710 cm$^{-1}$ in the polymer. No polymer formation was observed when PSK was absent in solution. In view of this discussion, the following mechanism (Scheme 1) is suggested.

## Mechanism (Scheme 1)

$$VO_2^+ + H_3O^+ \xleftrightarrow{K} V(OH)_3^{2+}$$

$$Ru(III) + V(OH)_3^{2+} \xleftrightarrow{K_1} Ru(IV) + V(IV)$$



$$C_6H_5-CH=CH-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 + Ru(IV) \xleftrightarrow{K_2} [C_6H_5-CH=CH-\overset{\overset{\displaystyle C_6H_5}{|}}{C}=O\cdots Ru(IV)]$$

(Adduct)

$$\text{Adduct} \xrightarrow[\text{slow}]{k} C_6H_5CH=\overset{+}{C}H + C_6H_5\dot{C}=0 + Ru(III)$$

$$C_6H_5CH=\overset{+}{C}H + H_2O \xrightarrow{\text{fast}} C_6H_5CH=CHOH + H^+$$

$$\text{keto-enol} \Updownarrow \text{tautomerism}$$

$$\underset{\text{phenylacetaldehyde}}{C_6H_5-CH_2-CHO}$$

$$C_6H_5-CH_2-CHO + 2V(V) \xrightarrow{\text{fast}} \underset{\text{phenyl acetic acid}}{C_6H_5CH_2COOH} + 2V(IV)$$

$$C_6H_5\dot{C}=O + V(V) + H_2O \xrightarrow{\text{fast}} \underset{\text{benzoic acid}}{C_6H_5COOH} + H^+ + V(IV)$$

This mechanism accounts for the rate law observed, radicals produced, and stoichiometry. The reason for enhancement in rate observed in V(V)-PSK reactions when Ru(III) was added is probably the higher oxidation potential of Ru(IV)-Ru(III) couple compared to V(V)-V(IV).

From the preceding mechanism, the following rate law was derived:

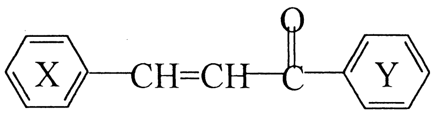
$$\text{rate} = \frac{-d[V(V)]}{dt} = \frac{kKK_1K_2[Ru(III)][PSK][V(V)][H^+]}{[V(IV)]}$$

where $VO_2^+$ is written as V(V) for simplicity.

Using Arrhenius plots, i.e., log $k$ vs. $1/T$, activation energies ($E_a$) have been evaluated, and using these $E_a$ values other activation parameters like $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ have been calculated and are given in the Table I. The $\Delta G^{\#}$ values are nearer, indicating a similar mechanism is operative in all the cases. The mixed trends in $\Delta S^{\#}$ values (positive and negative) obtained in the present study indicate that the transition state formed during the reaction varies from a rigid nature to a loosely bounded one, which could not be detected by the kinetic as well as the spectrophotometric method.

## Substituent Effects

The effect of substituents on the reaction rate was studied by varying the substituents in both the rings, i.e., X and Y of PSK (Structure 1). The order of reactivity with various substituents in ring X for any particular substituent in ring Y was $p$-$CH_3$ > $p$-Cl ≥ H > $p$-$NO_2$ ≥ $m$-Cl. The order of reactivity for substituents in ring Y for a particular substituent in ring X, varied with the type of substituent in ring X; for example, for $p$-$CH_3$ in ring X the order was $p$-Cl > $p$-$CH_3$ > H > $p$-$NO_2$ and for $p$-Cl the order is $p$-$CH_3$ > $p$-Cl > H > $p$-$NO_2$. When $p$-Cl was present in ring Y, it behaved as an electron-releasing group more efficiently when an electron-releasing group like $p$-$CH_3$ was present in ring X. The order of reactivity when substituents were H or $m$-Cl in ring X for various substituents in ring Y was $p$-$NO_2$ > $p$-$CH_3$ > H > $p$-Cl. Here it is seen that the presence of $p$-$NO_2$ in ring Y increased the rate. The order of reactivity for various substituents in any ring appears to depend on the type of substituent present in the other ring. But the general trend observed in most of the cases (at most of the temperatures also) is that electron-releasing groups increased the rate of the reaction while electron-withdrawing groups retarded the rate of the reaction.



**Structure 1**

The observed second-order rate constant ($k'' = k_{obs}/[PSK]$) for simple PSK at 308 K is $20.9 \times 10^{-3}$ lit $mol^{-1}$ $sec^{-1}$ (Table II). When a methyl group was introduced in the *para* position of ring Y with H in ring X the rate constant increased to $28.7 \times 10^{-3}$ lit $mol^{-1}$ $sec^{-1}$. When the methyl group was introduced at *para* position in ring X instead, the rate increased to 1513 $\times 10^{-3}$ lit $mol^{-1}$ $sec^{-1}$. When methyl groups were introduced in the *para* position in both the rings the rate increased further to $3311 \times 10^{-3}$ lit 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 a positive hyperconjugative effect, which dominates due to extended conjugation of the phenyl ring with $\rangle C=C \langle$, thus favoring a pro-

**Table I** Calculated Activation Parameters in Ru(III) Catalyzed Oxidation of Various Substituted PSKs by V(V) ([PSK] = 7.50 × $10^{-3}$ mol dm$^{-3}$; [V(V)] = 1.00 × $10^{-3}$ mol dm$^{-3}$; [$H_2SO_4$] = 2.00 mol dm$^{-3}$; [Ru(III)] = 5.25 × $10^{-7}$ mol dm$^{-3}$; [AcOH] = 80.0%; Temp = 298–313 K).

| Substituent in Ring X | Substituent in Ring Y | $E_a$ kJ mol$^{-1}$ | $\Delta H^{\#}$ kJ mol$^{-1}$ | $\Delta G^{\#}$ kJ mol$^{-1}$ | $\Delta S^{\#}$ J deg$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| *p*-$CH_3$ | *p*-$CH_3$ | 93.7 | 91.1 | 72.5 | 60.0 |
| | H | 116 | 113 | 74.5 | 125 |
| | *p*-Cl | 152 | 149 | 69.4 | 260 |
| | *p*-$NO_2$ | 41.7 | 39.2 | 78.3 | −127 |
| H | *p*-$CH_3$ | 91.0 | 88.4 | 84.7 | 12.0 |
| | H | 89.1 | 86.5 | 85.5 | 3.25 |
| | *p*-Cl | 71.2 | 68.7 | 86.4 | −57.5 |
| | *p*-$NO_2$ | 54.6 | 52.0 | 83.0 | −100 |
| *p*-Cl | *p*-$CH_3$ | 100 | 97.9 | 83.1 | 48.0 |
| | H | 97.1 | 94.5 | 84.8 | 31.5 |
| | *p*-Cl | 61.3 | 58.7 | 84.6 | −84.1 |
| | *p*-$NO_2$ | 91.2 | 88.6 | 85.4 | 10.4 |
| *p*-$NO_2$ | *p*-$CH_3$ | 54.7 | 52.2 | 86.4 | −111 |
| | H | 58.9 | 56.4 | 86.5 | −97.7 |
| | *p*-Cl | 73.2 | 70.6 | 86.9 | −52.9 |
| *m*-Cl | *p*-$CH_3$ | 38.8 | 36.3 | 86.3 | −162 |
| | H | 49.6 | 47.0 | 86.7 | −128 |
| | *p*-Cl | 51.5 | 48.9 | 87.1 | −124 |
| | *p*-$NO_2$ | 49.7 | 47.2 | 85.8 | −125 |

**Table II** Effect of Temperature and Substituents on $k''$ in Ru(III) Cat. Oxidation of PSKs by V(V) ([PSK] = 7.50 × $10^{-3}$ mol dm$^{-3}$; [V(V)] = 1.00 × $10^{-3}$ mol dm$^{-3}$; [$H_2SO_4$] = 2.00 mol dm$^{-3}$; [Ru(III)] = 5.25 × $10^{-7}$ mol dm$^{-3}$; [AcOH] = 80.0%)

| Substituent in Ring X | Substituent in Ring Y | $k'' \times 10^3$ lit mol$^{-1}$ sec$^{-1}$ | | | |
|---|---|---|---|---|---|
| | | **298 K** | **303 K** | **308 K** | **313 K** |
| *p*-$CH_3$ | *p*-$CH_3$ | 1006 | 2106 | 3311.3 | 6309.5 |
| | H | 339 | 758.6 | 1513.6 | 3162.3 |
| | *p*-Cl | 1694 | 4365.1 | 10964.8 | 31622.7 |
| | *p*-$NO_2$ | 192.5 | 257.0 | 331.3 | 426.6 |
| H | *p*-$CH_3$ | 9.3 | 16.6 | 28.7 | 53.1 |
| | H | 7.16 | 10.3 | 20.9 | 36.3 |
| | *p*-Cl | 6.9 | 11.7 | 15.3 | 28.8 |
| | *p*-$NO_2$ | 25.6 | 38.9 | 53.7 | 74.1 |
| *p*-Cl | *p*-$CH_3$ | 23.1 | 24.5 | 51.2 | 147 |
| | H | 8.96 | 21.7 | 26.9 | 64.6 |
| | *p*-Cl | 12.9 | 20.5 | 28.3 | 43.0 |
| | *p*-$NO_2$ | 6.26 | 10.6 | 21.1 | 34.9 |
| *p*-$NO_2$ | *p*-$CH_3$ | 7.67 | 11.52 | 14.0 | 23.1 |
| | H | 6.68 | 10.24 | 13.5 | 21.5 |
| | *p*-Cl | 4.47 | 7.24 | 11.6 | 18.3 |
| *m*-Cl | *p*-$CH_3$ | 7.04 | 9.97 | 14.7 | 15.3 |
| | H | 5.20 | 8.00 | 12.8 | 13.0 |
| | *p*-Cl | 4.50 | 6.50 | 11.0 | 11.5 |
| | *p*-$NO_2$ | 8.00 | 9.12 | 17.9 | 16.0 |

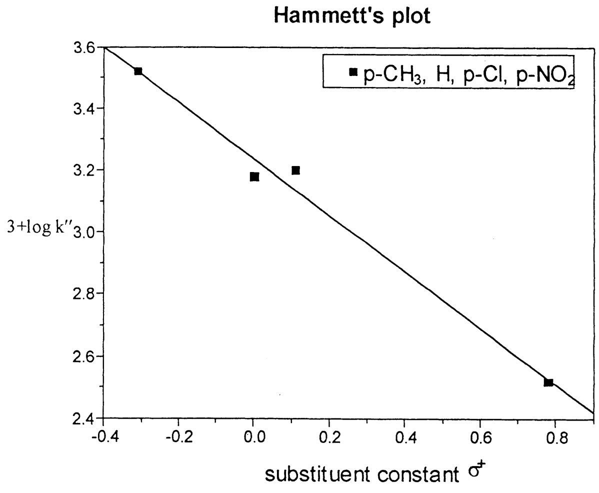


**Figure 3** A plot of log $k''$ vs. $\sigma^+$.

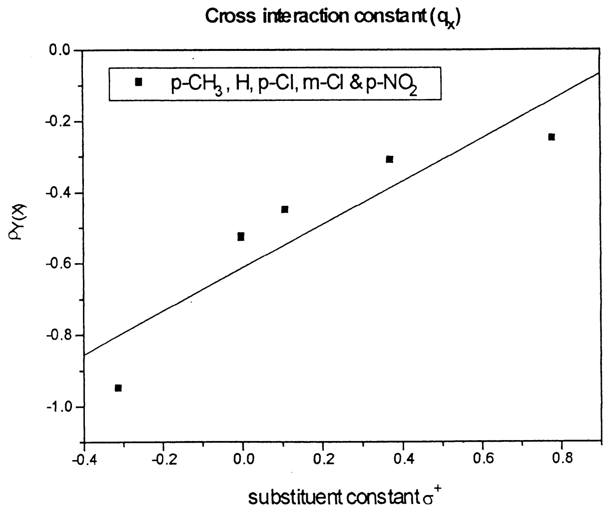


**Figure 4** A plot of $\rho_{Y(X)}$ vs. $\sigma^+$.

nounced electrophilic attack on >C=O group, compared to *p*-Me in ring Y. With *p*-NO$_2$ substituent in ring X the rate constant decreased ($k'' = 13.5 \times 10^{-3}$ lit mol$^{-1}$ sec$^{-1}$) probably due to −M effect (negative mesomeric effect). However, when the nitro group was present in *para* position in ring Y, the rate constant increased compared to simple PSK ($53.7 \times 10^{-3}$ lit mol$^{-1}$ sec$^{-1}$). The reason for this could be due to the −M effect of *p*-NO$_2$, resulting in the development of a partial positive charge at the carbonyl carbon, which, in turn, helps in drawing the electrons from the styryl group to make the carbonyl carbon slightly more electron rich compared to simple PSK. This probably facilitates the electron transfer from carbonyl oxygen to the Ru(IV) ion. With a electronegative atom like chlorine present in the *para* position in ring Y, the rate of oxidation is retarded compared to simple PSK, probably due to −I effect (negative inductive effect) of the group. The rate of oxidation with the *p*-Cl group in ring X is almost the same or slightly more than simple PSK, which could be due to the −I effect getting neutralized by the +M effect (positive mesomeric effect) as well as the effect of extended conjugation.

## Applicability of Interactive Free-Energy Relationship

The Hammett's reaction constant $\rho_{X(Y)}$ values have been calculated from the slope of the linear plot of log $k_{obs}$ vs. $\sigma$ (Fig. 3) for various substituents in ring X and for a given substituent in ring Y. They are for *p*-CH$_3$ (−0.550); H (−0.300) and *p*-Cl (−0.320) at 308 K. Similarly the $\rho_{Y(X)}$ values for various substituents

**Table III** Cross-Interaction Constants ($q_x$ and $q_y$) for Different Reactions

| Reaction | Site of Attack | $q_x$ | $q_y$ |
|---|---|---|---|
| 1. Oxidation of anils by acid bromate [19] | >C=N— in anils | 0.750 | 0.700 |
| 2. Os(VIII) catalyzed oxidation of PSKs by periodate [20] | >C=C< of PSK | 0.410 | 0.360 |
| 3. Os(VIII) catalyzed oxidation of PSKs by acid bromate | >C=C< of PSK | 0.917 | 1.02 |
| 4. Oxidation of PSKs by V(V) [5] | >C=O of PSK | 0.550 | 0.690 |
| 5. *Ru(III) catalyzed oxidation of PSKs by V(V) | >C=O of PSK | 0.600 | 1.00 |
| 6. Reduction of PSKs using cyclic voltametry | >C=C< of PSK | −0.671 | −0.672 |

* Present work.

in ring Y and for a particular substituent in ring X are $p$-$CH_3$ (−0.950); H (−0.525); $p$-Cl (−0.550); $m$-Cl (−0.310), and $p$-$NO_2$ (−0.275). The negative values obtained in all the cases indicate the 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 $\rho$ for various substituents in any particular ring is a function of the nature of substituents present in the other ring.

The results were analyzed in terms of interactive free-energy relationships for multiple substituent effects as discussed by Ruasse et. al [17,18] in 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 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 ring X and ring Y, respectively, with H in the other ring. $\sigma_x$ and $\sigma_y$ are the substituent constants of substituents in ring X and Y, respectively. This equation must be true whatever the nature of the substituent in ring X or Y, i.e., $q$ (which is called the cross-interaction constant) is expected to be the same. In the case of oxidation of aromatic anils by acid bromate [19] where the site of attack is $>C{=}N{-}$, $q_x$ and $q_y$ are expected to be same. In fact, the values reported, $q_x = 0.750$ and $q_y = 0.700$, are nearly the same, suggesting that the site of attack is indeed $>C{=}N{-}$. Similarly in the case of Os(VIII) catalyzed oxidation of PSKs by $IO_4^-$ [20], the cross-interaction constants obtained were $q_x = 0.41$ and $q_y = 0.36$, which are almost similar or very close. Here also the site of attack suggested was $>C{=}C<$. But in the oxidation of PSKs by V(V) where the site of attack is considered as $>C{=}O$, $q_x$ and $q_y$ were 0.550 and 0.690, respectively. It is reported earlier during the oxidation of PSKs by Ce(IV) [21] that $q_x$ and $q_y$ values differ considerably and the mechanism envisages a one-electron transfer from $>C{=}O$ group. In the present work, where the site of attack is considered as $>C{=}O$, $q_x$ and $q_y$ are not expected to be the same. The cross-interaction constants were calculated at four different temperatures: 298, 303, 308, and 313 K. The $q_x$ values were 0.575, 0.600, 0.625, and 0.600 (Fig. 4) and $q_y$ values were 0.850, 0.900, 0.950, and 1.00, respectively, at these temperatures, suggesting the site of attack is at $>C{=}O$. $q_x$ and $q_y$ values were positive for oxidation of PSKs by different oxidants and negative for the reduction process (Table III). This shows that the sign of $q$ could be used for distinguishing whether the reaction center is electron deficient (oxidation: $q = +ve$) or electron rich (reduction: $q = -ve$) in the transition state (Table IV).

**Table IV** Significance of $q$ in Oxidation and Reduction Reactions

| Process | Nature of Transition State | Sign of Hammett's $\rho$ Value | Sign of $q$ Value |
|---|---|---|---|
| oxidation | electron deficient | $-ve$ | $+ve$ |
| reduction | electron rich | $+ve$ | $-ve$ |

One of the authors (S.R.A.) is grateful to University Grants Commission for the award of a Senior Research Fellowship.

## BIBLIOGRAPHY

1. Djerassi, C; Engle, R. R. J Am Chem Soc 1953, 75, 3838.
2. Lee, D. G.; Van Den Engh, M. Oxidation in Organic Chemistry; Trahanovsky, W. S., Ed.; Academic Press: New York; Part B, Chapter 4.
3. Ramachandra, H.; Mahadevappa, D. S.; Rangappa, K. S. Indian J Chem 1997, 36B(4), 333.
4. Carlsen, P. H. J.; Katsaki, T.; Martin, V. S.; Sharpless, K. B. J Org Chem 1981, 46 (19), 3936.
5. Annapoorna, S. R.; Prasad Rao, M.; Sethuram, B. Indian J Chem 1998, 37B(9), 868.
6. Connick, R. E.; Fine, D. A. J Am Chem Soc 1960, 82, 4187.
7. Kohler, E. P. Organic Synthesis, Col, Vol I; Gilman, I., and Blatt, A. H., Eds.; John Wiley: New York, 1956; 78.
8. Vogel, A. I. Practical Organic Chemistry, Addison Wesley Longman Limited, 1971; 718.
9. Feigal, F. Spot Test in Organic Analysis; Elsevier: Amsterdam, 1966.
10. Waters, W. A.; Littler, J. W. Organic Chemistry, Vol 5-A; Wiberg, Kenneth B., Ed.; Academic Press: London, 1965.
11. Kemp, T. J.; Waters, W. A. J Chem Soc 1964, 339, 1192, 1610.
12. Murthy, G. S. S.; Sethuram, B.; Navaneeth Rao, T. Indian J Chem 1975, 13A, 849.
13. Murthy, G. S. S.; Sethuram, B.; Navaneeth Rao, T. Indian J Chem 1977, 15A, 880.
14. Cady, H. H.; Connick, R. E. J Am Chem Soc 1958, 80, 2646.

15. Connick, D. A.; Fine, F. A. J Am Chem Soc 1963, 83, 3414.
16. Wehner, Philip; Hindman, J. C. J Am Chem Soc 1950, 72, 3911.
17. Argile, A.; Ruasse, M. F. J Org Chem 1983, 48, 209.
18. Ruasse, M. F.; Argile, A. J Org Chem 1983, 48, 202.
19. Narsimha Char, P. Sondu, S.; Sethuram, B.; Navaneeth Rao, T. Indian J Chem 1988, 27A, 31.
20. Padmaja, S.; Nageswar Rao, K.; Prasad Rao, M.; Sethuram, B. Indian J Chem 1995, 34A, 351.
21. Sondu, S.; Sethuram, B.; Navaneeth Rao, T. Oxidation Comm 1987, 10, (3–4), 167.