

Oxygenation of Substituted (Phenylthio)acetic Acids by Acidic Bromate: A Kinetic and Mechanistic Study and Validity of Linear Free-Energy Relationships

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Kinetics and mechanistic investigations on the oxygenation of (phenylthio)acetic acid and its substituted compounds using bromate in acid medium have been carried out. The reaction exhibited first-order in [bromate], 1.6 order in [H₂SO₄], less than one order in [substrate] and displayed solvent isotopic effect of 1.75 (kD₂O/kH₂O). The reaction rate is not affected by ionic strength variation, however, enhanced by lowering dielectric constant of the medium. Structural modifications in the aryl moiety of the substrate resulted in a change of reactivity, where electron-seeking substituents decreased the reaction rate. The order of reactivity among the studied substrates is *para*-methoxy > *para*-methyl > -H > *para*-chloro ≈ *para*-bromo > *para*-nitro(phenylthio)acetic acid and showed an excellent correlation between rate constant and the Hammett substituent constant (σ value). The reaction constant (ρ) value is negative (-1.37 at 303 K) and decreased by increase in the reaction temperature. Proposed mechanism involves decomposition of the complex formed between acid bromate and the substrate. Based on the proposed mechanism, an appropriate rate law has been derived and tested for its validity. Activation parameters and isokinetic temperature have been evaluated and discussed. The validity of linear free-energy relationships have been discussed thoroughly.

Keywords: (Phenylthio)acetic acids, Acid Bromate, Kinetic study, Hammett constant, Oxygenation, Isokinetic relationship.

INTRODUCTION

Oxidation resulting oxygenation of compounds which selectively follow environmentally benign criteria is one of the effective ways for the oxo-functionalization of organic compounds. The main interest lies in the oxygenation of biologically significant organic sulfides such as (phenylthio)acetic acids using oxo-oxidants. Literature survey reveal that oxidation of (phenylthio)acetic acids using periodic acid and RuO₄ catalyst [1], permanganate [2], potassium peroxydisulfate [3], peroxomonophosphoric acid [4], potassium peroxydiphosphate [5], perborate [6,7], *N*-chlorosaccharin [8], *etc.* were carried out and different mechanisms pertaining to oxygen atom transfer from the oxidant to the substrate have been presented. However, none of them showed satisfactory results and found unsuitable for oxygenation of (phenylthio)acetic acids due to low conversion, formation of several by products, decomposition of oxidants, *etc.* Hence, it is necessary to find out an efficient oxo-oxidant that can oxygenate (phenylthio)acetic

acids to a maximum yield without interference of the reduction product of oxidant.

Oxidants such as potassium bromate and sodium bromate are innocuous, inexpensive, stable solids and easy to handle. Since Br⁻ ion is the reduction product of bromate oxidation, which makes bromate oxidations environmentally benign unlike other oxidations. On the other hand, potassium bromate is a mild and selective oxidizing agent, which oxidizes amines to azo compounds [9], oximes to carbonyl compounds [10], and is widely used in the oxidation of various organic substrates [11-14]. Since there is no report on the oxidation/oxygenation of (phenylthio)acetic acids by bromate and as a part of our ongoing bromate oxidations [15-19], we herein report the kinetics of oxygenation of substituted (phenylthio)acetic acids by bromate in acid medium emphasizing on the mechanistic aspects and also on structure- reactivity correlation.

The main objectives of this study are to identify the reactive species of substrate and oxidant, interpreting a possible mechanism for the reaction, obtaining appropriate rate law, identi-

fying and estimation of the reaction products, evaluation of related kinetic, thermodynamic parameters and verifying the linear free-energy and isokinetic relationships.

EXPERIMENTAL

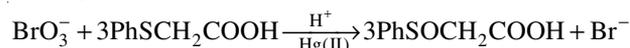
From the standard procedure, using chloroacetic acid and the corresponding thiophenols, (phenylthio)acetic acid and (substituted phenylthio)acetic acids were prepared in alkaline medium [3]. Analytical grade KBrO_3 (Reidal), H_2SO_4 and mercuric acetate (Merck) were used. D_2O (99.4% pure) was procured from the BARC, Mumbai, India. Acetic acid (BDH, AR) was purified by refluxing with chromic acid. All other reagents used were of AR grade. Solutions were prepared either with double distilled water or acetic acid (purified) and standardized.

Kinetic measurements: All the kinetic studies were performed under pseudo-first-order conditions with ten-fold excess of [substrate] over [bromate] at a fixed temperature ($\pm 0.1^\circ\text{C}$). Initiation of reaction was done by the addition of requisite amounts of potassium bromate to reaction mixtures containing the required amount of all other reagents and the reaction was monitored by determination of unconsumed [bromate] using iodometric method. From the plots of \log [bromate], against time, pseudo-first order rate constants (k , s^{-1}) were obtained, which were reproducible with $\pm 5\%$. The possible side reactions were avoided throughout the study by using freshly prepared solutions. During the reaction, molecular bromine production and its resultant reaction with (phenylthio)acetic acid was eliminated by adding mercuric acetate, a bromo complexing agent [15]. An optimum concentration of 0.005 M mercuric acetate has been used to keep back all the bromide ions. Hence, the reported rate constants and thermodynamic parameters pertain to pure bromate oxidation only.

Product analysis: The reaction mixture was held overnight and the solvent was extracted by distillation under reduced pressure. The residue was then extracted with ether and dried over anhydrous Na_2SO_4 before being subjected to TLC analysis in a solvent system of *n*-butanol, water and acetic acid (4:5:1 upper layer) where the residue gave two spots (which were made visible by exposure to iodine) corresponding to (phenylthio)acetic acid ($R_f = 0.84$) and phenylsulfinylacetic acid ($R_f = 0.45$) respectively, there by confirming phenylsulfinylacetic

acid as the reaction product. The IR spectrum of the obtained product revealed a strong absorption band at 1050 cm^{-1} , which pertains to $\text{S}=\text{O}$ stretching and the IR spectrum is super-imposable with that of an authentic sample of phenylsulfinylacetic acid [8,20]. The oxidation products of other (*para*-substituted phenylthio)acetic acids were confirmed to be the corresponding phenylsulfinylacetic acids.

Stoichiometry: Equilibrating the reacting mixture of different ratios of [bromate] and [(phenylthio)acetic acid] at 30°C for 24 h, all other reagents being kept constant, the stoichiometry of the reaction was determined. Iodometric estimation of unconsumed bromate indicates that one mole of bromate used three moles of (phenylthio)acetic acid as shown in the given equation:



RESULTS AND DISCUSSION

Effect of various parameters: The disappearance rate of [bromate] followed first order kinetics, when concentrations of all other reagents being kept constant and [substrate] \gg [bromate], which was confirmed from the linear plots of \log [bromate], against time. Pseudo first-order rate constants (k , s^{-1}), obtained from the slopes of such plots remained unchanged (Table-1) with the variation of [bromate], further confirming first order kinetics of the rate on [bromate].

To analyze the influence of [(phenylthio)acetic acid] on the rate, the reaction was studied in the concentration range of 0.01-0.1 M (Table-1). $\log k$ versus \log [substrate] plots were linear with slopes less than unity (0.80-0.89). Linear Plots of $1/k$ versus $1/[\text{substrate}]$ (Fig.1) with varying intercepts also confirmed less than unity order in [substrate].

The increase in reaction rate (Table-1) with increase in [acid], at constant concentration of all other reagents revealed second order (1.6-1.8) dependence on [acid]. Influence of ionic strength on the reaction rate was studied by varying $[\text{NaClO}_4]$ and has no discernible impact on the reaction rate, hence the ionic strength of the medium was not maintained at any constant value.

The influence of dielectric constant of medium on the reaction rate was studied by varying the composition of acetic

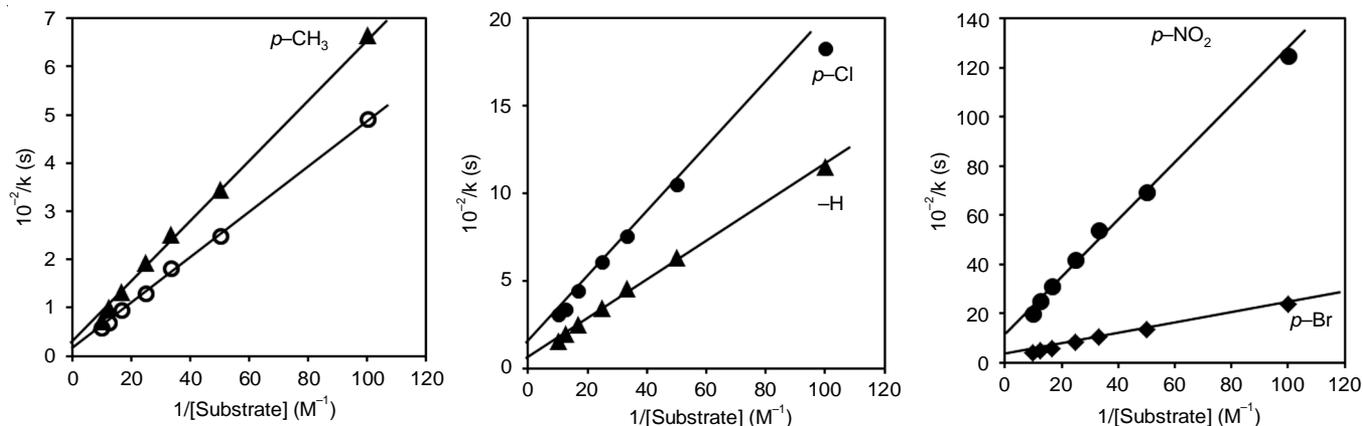


Fig. 1. Plot between $1/k$ and $1/[\text{substrate}]$

| TABLE-1 FACTORS INFLUENCING THE OXYGENATION RATE OF (PHENYLTHIO)ACETIC ACIDS BY BROMATE IN ACID MEDIUM AT 303 K | | | | | | | |
|--|---|---|----------------------------|---------------------------|--------------|--------------|---------------------------|
| Non-variable constituent (mol dm ⁻³) | Variable constituent (mol dm ⁻³) | 10 ⁵ × k (s ⁻¹) ^a | | | | | |
| | | -H | <i>p</i> -OCH ₃ | <i>p</i> -CH ₃ | <i>p</i> -Cl | <i>p</i> -Br | <i>m</i> -NO ₂ |
| [Bromate] | | | | | | | |
| [Substrate] = 0.02 [H ₂ SO ₄] = 0.20 AcOH-H ₂ O = 1:1 (% v/v) [Hg(OAc) ₂] = 0.005 | 4.0 × 10 ⁻⁴ | 15.83 | 40.13 | 28.93 | 9.52 | 7.44 | 1.42 |
| | 6.0 × 10 ⁻⁴ | 15.85 | 40.16 | 28.94 | 9.56 | 7.42 | 1.45 |
| | 8.0 × 10 ⁻⁴ | 15.84 | 40.14 | 28.96 | 9.53 | 7.44 | 1.44 |
| | 10.0 × 10 ⁻⁴ | 15.85 | 40.14 | 28.94 | 9.53 | 7.43 | 1.44 |
| | 12.0 × 10 ⁻⁴ | 15.86 | 40.15 | 28.92 | 9.56 | 7.43 | 1.46 |
| | 16.0 × 10 ⁻⁴ | 15.85 | 40.13 | 28.95 | 9.54 | 7.45 | 1.45 |
| | 20.0 × 10 ⁻⁴ | 15.84 | 40.14 | 28.93 | 9.53 | 7.42 | 1.44 |
| [Substrate] | | | | | | | |
| [Bromate] = 1.0 × 10 ⁻³ [H ₂ SO ₄] = 0.20 AcOH-H ₂ O = 1:1 (% v/v) [Hg(OAc) ₂] = 0.005 | 1.0 × 10 ⁻² | 8.71 | 20.29 | 15.04 | 5.47 | 4.20 | 0.80 |
| | 2.0 × 10 ⁻² | 15.85 | 40.13 | 28.94 | 9.53 | 7.43 | 1.44 |
| | 3.0 × 10 ⁻² | 21.88 | 54.95 | 39.81 | 13.18 | 9.55 | 1.86 |
| | 4.0 × 10 ⁻² | 28.84 | 76.14 | 52.13 | 16.47 | 12.13 | 2.39 |
| | 6.0 × 10 ⁻² | 39.81 | 104.72 | 75.85 | 22.38 | 16.98 | 3.24 |
| | 8.0 × 10 ⁻² | 51.28 | 142.10 | 100.00 | 29.65 | 20.44 | 3.97 |
| | 10.0 × 10 ⁻² | 63.09 | 169.37 | 137.67 | 32.67 | 25.00 | 5.00 |
| [H ₂ SO ₄] | | | | | | | |
| [Bromate] = 1.0 × 10 ⁻³ [Substrate] = 0.02 AcOH-H ₂ O = 1:1 (% v/v) [Hg(OAc) ₂] = 0.005 | 0.10 | 5.24 | 12.08 | 9.55 | 3.02 | 2.48 | - |
| | 0.20 | 15.85 | 40.13 | 28.94 | 9.53 | 7.43 | 1.42 |
| | 0.40 | 47.86 | 125.89 | 87.10 | 30.20 | 22.30 | 4.27 |
| | 0.60 | 95.50 | 251.18 | 158.28 | 55.00 | 47.86 | 7.95 |
| | 0.80 | 138.03 | 398.10 | 252.20 | 87.10 | 66.90 | 12.80 |
| | 1.00 | 199.52 | - | - | 125.89 | 95.50 | 17.86 |
| AcOH-H ₂ O (%v/v) | | | | | | | |
| [Bromate] = 1.0 × 10 ⁻³ [Substrate] = 0.02 [H ₂ SO ₄] = 0.20 [Hg(OAc) ₂] = 0.005 | 30-70 (55.59) ^b | 7.58 | 16.98 | 14.12 | 4.26 | 3.23 | - |
| | 40-60 (48.53) | 10.47 | 23.90 | 18.19 | 6.17 | 4.46 | 0.89 |
| | 50-50 (41.48) | 15.85 | 40.13 | 28.94 | 9.53 | 7.43 | 1.44 |
| | 60-40 (34.30) | 28.18 | 74.10 | 50.11 | 15.85 | 13.18 | 2.82 |
| | 70-30 (27.02) | 70.79 | 199.52 | 112.20 | 39.81 | 35.48 | 8.51 |

^aReported rate constants are the mean of duplicate experiments; ^bValues in parentheses indicate dielectric constant of the medium.

acid and water. Increase in dielectric constant of the medium (D) decreased the reaction rate (Table-1) and the plots of log k versus 1/D were found to be linear with positive slopes (Fig. 2). The performed blank experiments inferred that acetic acid was not oxidized by bromate under these reaction conditions. The result therefore truly represents the rates under different dielectric medium of the solution.

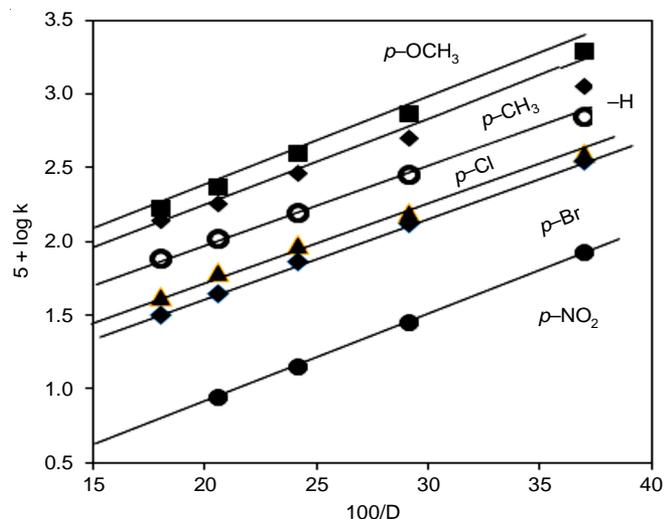


Fig. 2. Plot between log k and 1/D

The reactions were studied by changing the concentrations of acrylonitrile from 0.1-1.0 M to examine the interference of free radicals. There was no effect of added acrylonitrile on the reactions rate. Also, no precipitate was observed due to polymerization of acrylonitrile, suggesting the absence of any free radical formation in the reaction.

Enhancement of rate in the D₂O medium (k(D₂O)/k(H₂O) = 1.75 at 303 K) is because of D₃O⁺, which is almost three times stronger acid than H₃O⁺ [21,22] and the present solvent isotope effect suggests a proton catalyzed oxidation reaction.

The reaction was carried out in the temperature range of 303-323K, where concentrations of all other reagents were kept constant (Table-2). Activation energy (E_a) of the reactions was calculated from the plot of log k versus 1/T and corresponding thermodynamic parameters viz. enthalpy of activation (ΔH[‡]) entropy of activation (ΔS[‡]) and Gibbs free-energy of activation (ΔG[‡]) were calculated (Table-2). A fair correlation between the activation enthalpies and entropies suggests a compensation effect [23,24]. The plot of ΔH[‡] against ΔS[‡] was linear (Fig. 3a) and the isokinetic temperature (β) is found to be 363.5 K. The isokinetic temperature calculated from the Exner's plot (Fig. 3b) of log k_{313 K} versus log k_{323 K} is 365 K, which is in excellent coincidence with the β value observed from the ΔH[‡] against ΔS[‡] plot.

TABLE-2
INFLUENCE OF TEMPERATURE AND THERMODYNAMIC PARAMETERS FOR THE
OXYGENATION OF (PHENYLTHIO)ACETIC ACIDS BY ACIDIC BROMATE

| Temp. (K) | $10^5 \times k \text{ (s}^{-1}\text{)}^a$ | | | | | |
|--|---|----------------------------|---------------------------|--------------|--------------|---------------------------|
| | -H | <i>p</i> -OCH ₃ | <i>p</i> -CH ₃ | <i>p</i> -Cl | <i>p</i> -Br | <i>m</i> -NO ₂ |
| | (1.4661) ^b | (1.435) | (1.445) | (1.474) | (1.477) | (1.535) |
| 303 | 15.85 | 40.13 | 28.94 | 9.53 | 7.43 | 1.44 |
| 308 | 21.49 | 46.25 | 31.88 | 12.87 | 11.20 | 2.89 |
| 313 | 29.20 | 52.58 | 37.13 | 16.43 | 15.00 | 4.98 |
| 323 | 42.41 | 65.66 | 45.32 | 24.66 | 22.33 | 8.55 |
| <i>E</i> _a (kJ mol ⁻¹) | 39.25 | 20.10 | 18.23 | 40.21 | 44.03 | 72.75 |
| ΔH^\ddagger (kJmol ⁻¹) | 36.73 | 17.58 | 15.72 | 37.69 | 41.52 | 70.23 |
| ΔS^\ddagger (J mol ⁻¹ K ⁻¹) | -196.6 | -252.1 | -261.0 | -197.7 | -187.1 | -104.1 |
| ΔG^\ddagger (kJ mol ⁻¹) | 96.29 | 93.98 | 94.80 | 97.59 | 98.22 | 102.39 |

Experimental conditions: [substrate] = 0.02 mol dm⁻³, [bromate] = 0.001 mol dm⁻³, [H₂SO₄] = 0.20 mol dm⁻³, [Hg(OAc)₂] = 0.005 mol dm⁻³, HOAc-H₂O = 1:1 (% v/v). ^aThe average error in rate constant is $\pm 5\%$. ^bData in parentheses are the oxidation potentials of substituted (phenylthio)acetic acids estimated by using Marcus equation [Ref. 8,24].

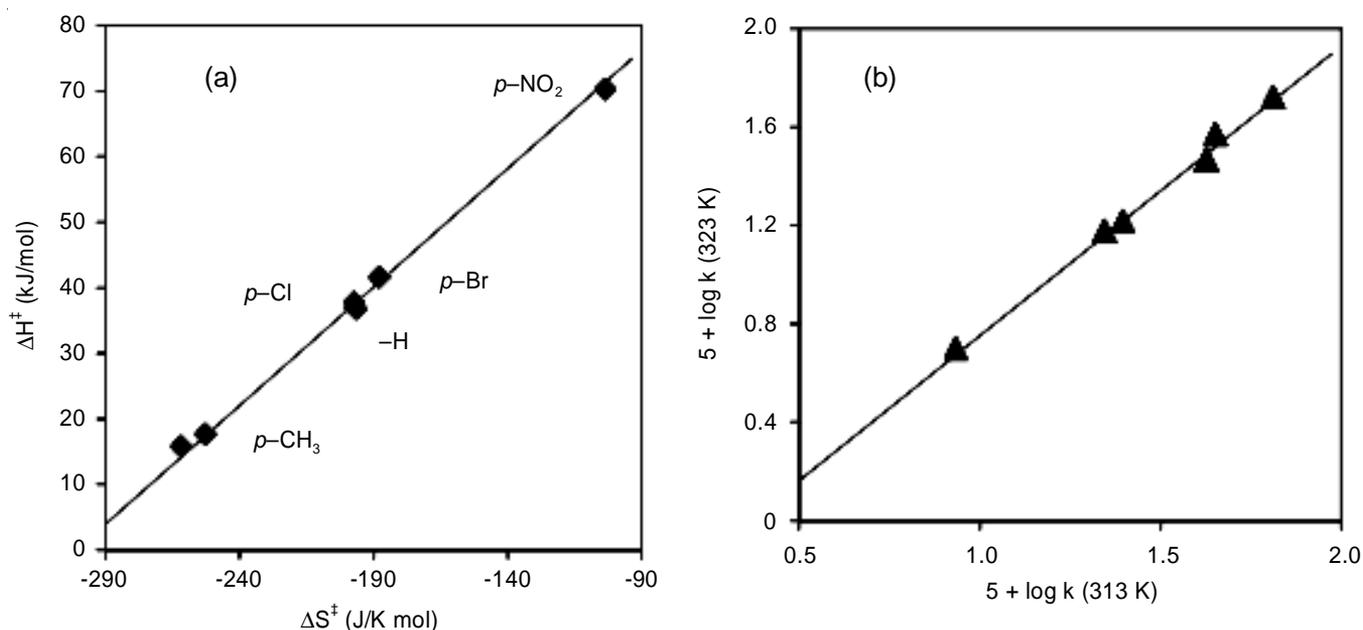


Fig. 3. Plot of (a) ΔH^\ddagger versus ΔS^\ddagger and (b) $\log k_{323\text{ K}}$ against $\log k_{313\text{ K}}$ (reaction conditions as in Table-2)

The influence of substituent on the rate of reaction was studied by using different *para* substituted (phenylthio)acetic acids at various temperatures. Structural modifications in the aryl moiety of substrate resulted in varied reactivity. Electron-donating substituents (donors) increased the reaction rate and electron-seeking groups (acceptors) decreased the rate. The reactivity order of different (arylythio)acetic acids is as: *para*-OCH₃ > *para*-CH₃ > -H > *para*-Cl \approx *para*-Br > *para*-NO₂ (phenylthio)acetic acid. The Hammett's plot of $\log k$ versus σ (substituent constant) for the studied reaction is linear with excellent correlation coefficient ($R^2 \geq 0.987$) at all the investigated temperatures (Fig. 4). The obtained reaction constants (ρ) are negative and decrease (in magnitude) with increase in temperature (Table-3).

Active species of the reactants: In bromate oxidations, the most likely reactive species are BrO₃⁻ and protonated [18] bromate (HBrO₃ or H₂Br⁺O₃/Br⁺O₂) in acidic medium. Therefore, the present oxidation reaction may be a reaction involving one of the reactive species. The effect of solvent polarity and

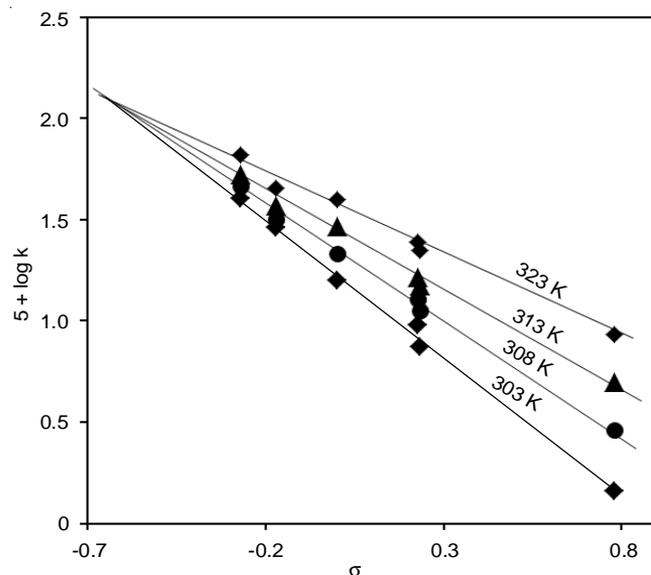


Fig. 4. Plot of $\log k$ against σ

TABLE-3
SOLVENT ISOTOPE EFFECT IN THE
OXYGENATION OF (PHENYLTHIO)ACETIC
ACIDS BY ACIDIC BROMATE AT 303 K

| Substituent | $10^5 \times k$ (H ₂ O) (s ⁻¹) | $10^5 \times k$ (D ₂ O) (s ⁻¹) | k (D ₂ O)/ k (H ₂ O) |
|-------------------|--|--|---|
| -H | 15.85 | 27.74 | 1.75 |
| <i>p</i> -Methoxy | 40.13 | 70.62 | 1.76 |
| <i>p</i> -Methyl | 28.94 | 50.65 | 1.75 |
| <i>p</i> -Chloro | 9.53 | 17.15 | 1.80 |
| <i>p</i> -Bromo | 7.43 | 13.00 | 1.75 |
| <i>p</i> -Nitro | 1.44 | 2.57 | 1.78 |

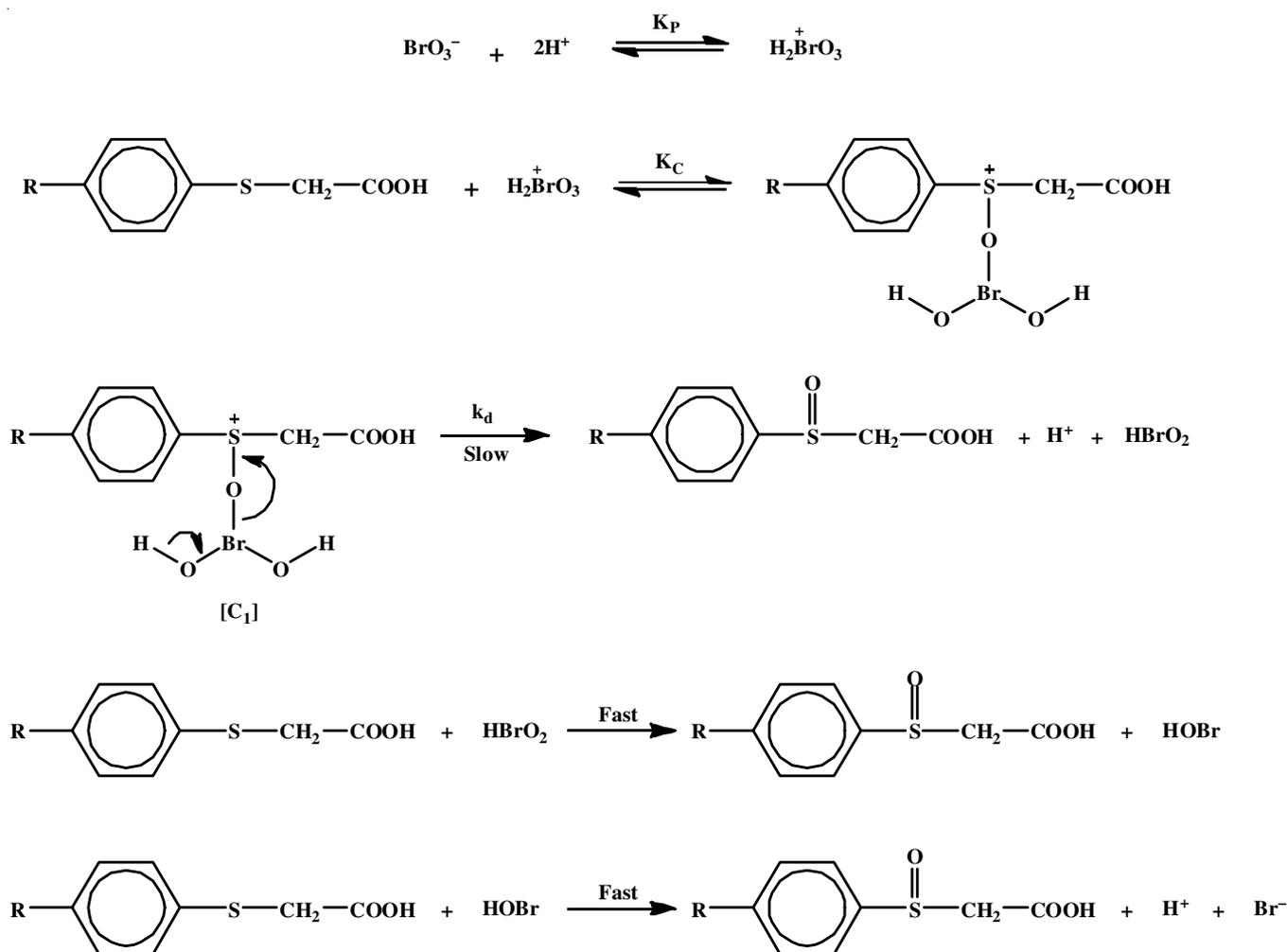
Experimental condition as in Table-1.

increase in rate with increase in [H₂SO₄] reduce the likelihood of unprotonated bromate (BrO₃⁻) to be the reactive species. Amis *et al.* [25] proposed Br⁺O₂ as one such oxidizing species. Several researchers [15,26-28] suggested that in moderately strong acid solutions active species of bromate is H₂Br⁺O₃ with a protonation constant of 0.201 dm⁶ mol⁻². This is further supported by the influence of solvent where the reaction rate increased with an increase in the amount of acetic acid and also from the linear plots of log *k* versus 1/*D* (Fig. 2). The positive slope of the plot indicates an interaction between a

positive ion and a dipole molecule, thus suggesting H₂Br⁺O₃ as the reactive species of bromate. The enhanced rate with an increase in [acid] and second order in [acid] also confirms that H₂Br⁺O₃ is involved as reactive species in the oxidation of (phenylthio)acetic acids.

The existence of PhSCH₂COO⁻ in acidic solution does not occur as the dissociation of (phenylthio)acetic acid is completely suppressed. Therefore, the undissociated form of the substrate can be taken as the only form in acidic media. Also, a fair intercept in the plot of 1/*k* against 1/[substrate] suggests Michaelis-Menten type dependability of reaction rate (Fig. 1) and indicates complex formation between the reactive species of oxidant and the substrate.

Mechanism: Based on the above discussion and in agreement with experimental results, the mechanism for the bromate oxygenation of (phenylthio)acetic acid has been proposed (**Scheme-I**). The reaction pathway involves formation of an ester intermediate (C1) in a fast pre-equilibrium step by the electrophilic attack of H₂Br⁺O₃ on the sulfur utilizing the unshared pair of electrons, and its slow decomposition to products. The negative ρ value for the reaction suggests that the transition state is electron seeking when compared to the sulfide. Donation of unshared pair [29] of electrons to bromate result in the



Scheme-I

formation of a covalent bond and consequently sulfur becomes a positively charged center (in agreement with the negative Hammett ρ value). Hence, the oxidation involves a direct oxygen transfer from bromate to the sulfur atom of (phenylthio)acetic acid resulting in phenylsulfinylacetic acid as the reaction product in quantitative yield (90-96%).

HBrO₃ is strong enough and consumes the substrates (**Scheme-I**) and oxidizes them in fast steps and finally converts to bromide ion, thus inferring 1:3 (oxidant:substrate) stoichiometry.

Rate law: Based on the proposed mechanism as shown by **Scheme-I**, the rate in terms of [bromate] can be given as:

$$\text{Rate} = \frac{-d[\text{BrO}_3^-]}{dt} = k_d[C_1] \quad (1)$$

On the basis of the steps in **Scheme-I**, eqns. 8 & 9 can be obtained as follows:

$$[C_1] = K_p K_c [\text{substrate}][\text{BrO}_3^-][\text{H}^+]^2 \quad (2)$$

Upon substitution of eqn. 2 in eqn. 1, we get eqn. 3:

$$\text{Rate} = \frac{-d[\text{BrO}_3^-]}{dt} = k_d K_p K_c [\text{substrate}][\text{BrO}_3^-][\text{H}^+]^2 \quad (3)$$

As bromate exists in complexed and uncomplexed forms, concentration of bromate can be given by eqn. 4:

$$[\text{Br(V)}]_T = [\text{BrO}_3^-] + [\text{H}_2\text{Br}^+\text{O}_3] + [C_1] \quad (4)$$

$$[\text{Br(V)}]_T = [\text{BrO}_3^-] + K_p [\text{BrO}_3^-][\text{H}^+]^2 + K_p K_c [\text{substrate}][\text{BrO}_3^-][\text{H}^+]^2 \quad (5)$$

$$[\text{Br(V)}]_T = [\text{BrO}_3^-] \{1 + K_p [\text{H}^+]^2 + K_p K_c [\text{substrate}][\text{H}^+]^2\} \quad (6)$$

Therefore,

$$[\text{BrO}_3^-] = \frac{[\text{Br(V)}]_T}{1 + K_p [\text{H}^+]^2 + K_p K_c [\text{substrate}][\text{H}^+]^2} \quad (7)$$

In terms of total bromate concentration the rate law can be given as eqn. 8:

$$\text{Rate} = \frac{-d[\text{Br(V)}]_T}{dt} = \frac{k_d K_p K_c [\text{substrate}][\text{H}^+]^2 [\text{Br(V)}]_T}{1 + K_p [\text{H}^+]^2 + K_p K_c [\text{substrate}][\text{H}^+]^2} \quad (8)$$

The rate law is in accordance with the observed experimental results explaining first order in [bromate], less than second order (1.6-1.8) in [H⁺] and Michaelis-Menten type kinetics of rate on [substrate]. It is relevant to point out that the oxidation occurs in the presence of sulfuric acid and in its absence the reaction does not occur.

Rate law (eqn. 8) upon rearrangement to equations (9-11) can be given as:

$$\frac{\text{Rate}}{[\text{Br(V)}]_T} = k(s^{-1}) = \frac{k_d K_p K_c [\text{substrate}][\text{H}^+]^2}{1 + K_p [\text{H}^+]^2 + K_p K_c [\text{substrate}][\text{H}^+]^2} \quad (9)$$

$$\frac{1}{k} = \frac{1}{k_d K_p K_c [\text{substrate}][\text{H}^+]^2} + \frac{1}{k_d K_c [\text{substrate}]} + \frac{1}{k_d} \quad (10)$$

$$\frac{1}{k} = \frac{1}{\{k_d K_p K_c [\text{H}^+]^2 + k_d K_c\} [\text{substrate}]} + \frac{1}{k_d} \quad (11)$$

Other conditions being stable, $1/k$ versus $1/[\text{substrate}]$ should be a straight line with a definite intercept on the $1/k$ axis, according to eqn. 11 and the validity of the proposed mechanism (**Scheme-I**) and rate law (eqn. 8) is supported by such a realization (Fig. 1). Influence of solvent on the reaction rate also supports the proposed mechanism. Due to charge dispersal, the intermediate complex C₁ is less polar than the reactants; hence, lowering the polarity of the solvent media is required to stabilize the complex C₁ over the reactants, thus increasing the reaction rate [18]. Such influence of the solvent can be observed from Table-1. Positive values of the evaluated thermodynamic parameters *viz.* free energy of activation and enthalpy of activation imply that the transition state is strongly solvated and negative entropy of activation indicates the formation of a compact activated complex with fewer degrees of freedom.

Protonation constant (K_p) of bromate has been calculated as 0.20 dm⁶ mol⁻² [15]. The decomposition constant (k_d) and complexation constant (K_c) have been calculated (Table-4) from the intercept and slope data of $1/k$ versus $1/[\text{substrate}]$ and $1/k$ against $1/[\text{H}^+]^2$ plots. Rate constants were calculated from the evaluated values of k_d, K_p and K_c under experimental conditions using eqn. 9, and the results were compared with experimental values. There is a high level of consensus between them (within ±5% error). This adds to the credibility of the proposed reaction mechanism (**Scheme-I**).

TABLE-4
DECOMPOSITION CONSTANT (k_d) AND COMPLEX FORMATION CONSTANT (K_c) VALUES FOR THE OXYGENATION OF (PHENYLTHIO)ACETIC ACIDS BY ACIDIC BROMATE

| Substituent | 10 ⁴ × k _d (s ⁻¹) | K _c |
|-------------------|---|----------------|
| -H | 20.0 | 736 |
| <i>p</i> -Methoxy | 66.6 | 1145 |
| <i>p</i> -Methyl | 40.0 | 950 |
| <i>p</i> -Chloro | 8.33 | 402 |
| <i>p</i> -Bromo | 5.55 | 364 |
| <i>p</i> -Nitro | 0.91 | 114 |

Experimental conditions as in Table-1.

Structural influences and linear free energy relationships: Study of the substituent effect will reveal more about nature of the transition state and thus the mechanism. Hence, kinetic studies were performed at four temperatures with a variety of (*para*-substituted phenylthio)acetic acids (Table-2). The reactivity of substrates is in the order of *para*-OCH₃ > *para*-CH₃ > -H > *para*-Cl ≈ *para*-Br > *para*-NO₂ (phenylthio)acetic acid. The plot between log k and substituent constant (σ) is linear (Fig. 4) at 303 K, with a negative slope value of -1.37, suggesting more positively charged sulfur centre in the transition state than when it is the reactant of the reaction [20]. The ρ value of the reaction at various temperatures ranged from -1.37 to -0.86 (Table- 3). In addition, the plot between log k and the oxidation potential (E_{ox}) of (phenylthio)acetic acids determined from the kinetic data in terms of Marcus equation [30-32] is found to be linear (Table-2) with a negative slope (Fig. 5). Since these quantities are interdependent, the

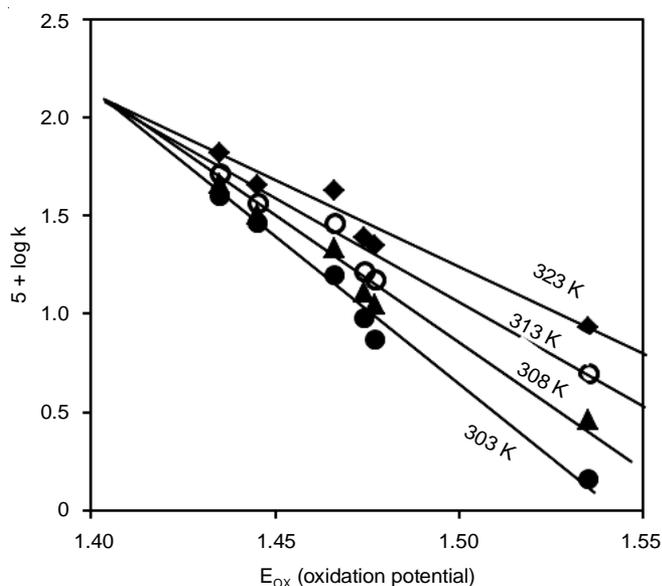


Fig. 5. Plot between $\log k$ and oxidation potential (E_{ox})

association between ΔH^\ddagger and ΔS^\ddagger should be viewed with scepticism. The isokinetic relationship could, however, be implicitly verified using the Exner plot [33] of $\log k_{313\text{ K}}$ versus $\log k_{323\text{ K}}$ which is found to be linear (Fig. 3b), with an excellent correlation coefficient (0.996) with a β value of 365 K. The linearity in Exner plot indicates that these reactions have a similar mechanism [34]. This is also supported by the near-consistency of ΔG^\ddagger values.

The reaction constant (ρ) is a measure of extent of electron requirement at the reaction centre and found to decrease in magnitude with increase in temperature. The negative value of ρ suggests the sensitivity of reaction to the steric effects and also provides information about the nature of transition

state involved during the reaction. A reaction involving positive charge development in the transition state is aided by electron-releasing substituents and ρ value will be negative [35], as is in the present case. The activation parameters are in favour of this view. The ΔH^\ddagger value is seen to decrease with increasing electron-donating ability of the substituents (Table-2), whereas, ΔS^\ddagger becomes more negative, reflecting a more solvated transition state. The methoxy substituent at the *para*-position does not show exalted reactivity and the nitro substituent fails to exhibit unduly suppressed rate. The rate of reaction correlates excellently with the usual Hammett σ value. The correlation in Exner's scale is also excellent. These observations indicate that conjugation/mesomeric effects are unlikely during the oxidation, only the inductive effect [36] of substituents predominate on the rate of reaction. The ρ value (-0.86 to -1.37) in the present study may be attributed to the nature of observed rate constant (k , s^{-1}), which is composite of several terms like protonation, complexation, oxidation, etc.

The linear plot of $\log K_C$ versus σ (Fig. 6a) and the linearity in the plot of $\log k_d$ versus σ (Fig. 6b) further support the electronic effect in the transition state and also suggests that all the (substituted phenylthio)acetic acids follow similar mechanism. From the plot of ρ against $1/T$ (Fig. 7) the isokinetic temperature (β) is found to be 365 K, which is in close agreement with the value obtained from the slope of the Exner's plot (364.5 K). It is interesting that although the rate constant is composite involving multi-reaction steps, an anti-compensation effect is not observed [19].

Conclusion

In an aqueous acetic acid medium containing H_2SO_4 , the oxygenation mechanism of several *para*-substituted (phenylthio)acetic acids using acid bromate was investigated. (Aryl-

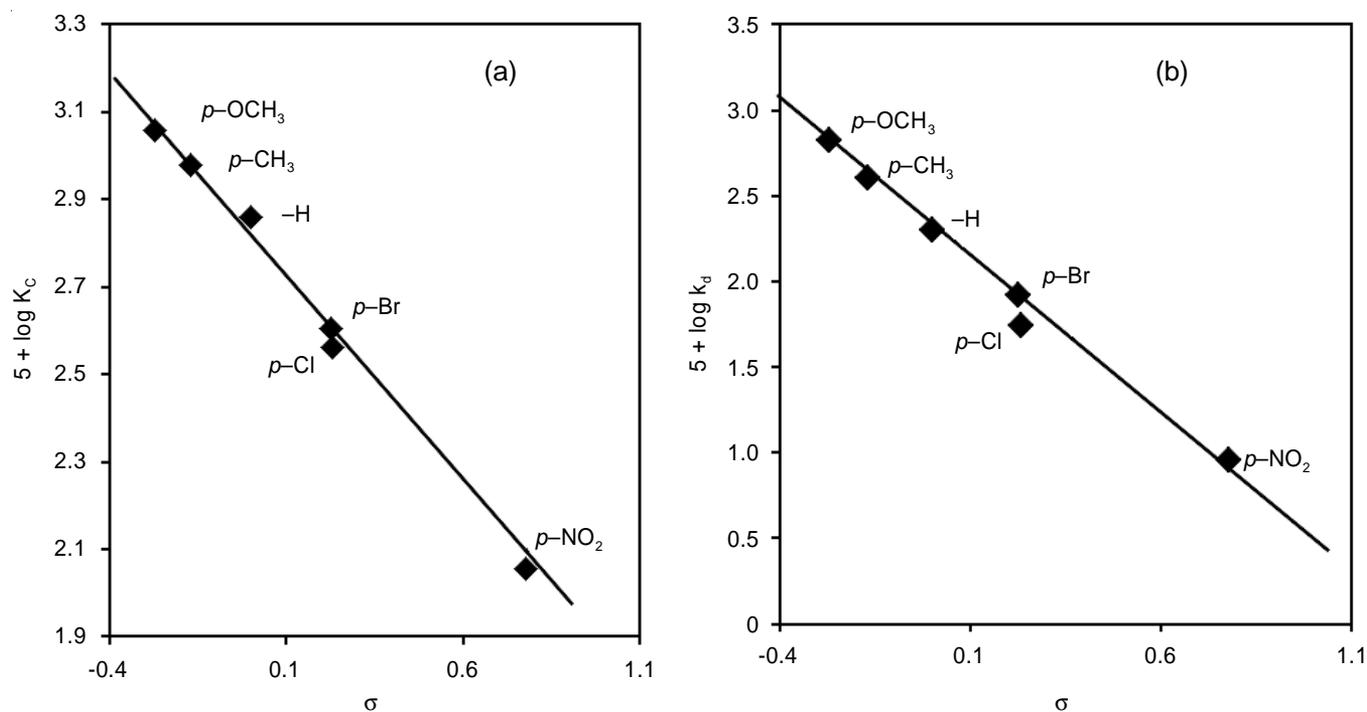


Fig. 6. Plot of (a) $\log K_C$ versus σ and (b) $\log k_d$ against σ

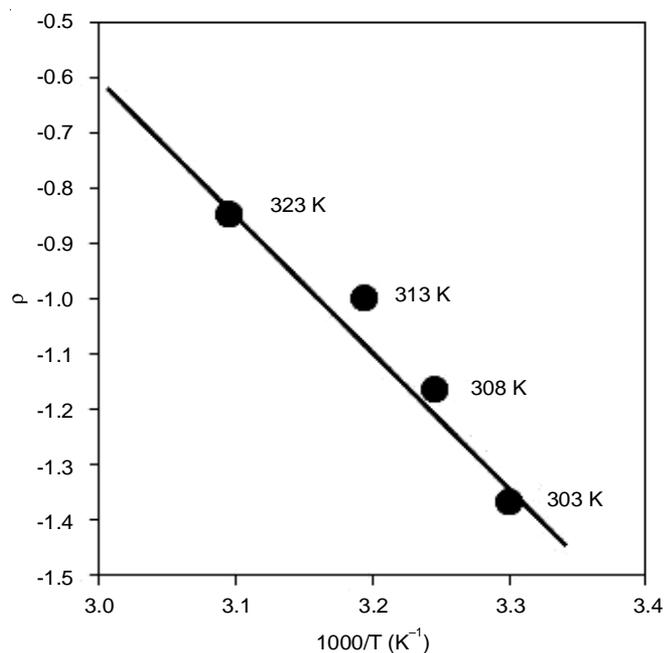


Fig. 7. Plot between reaction constant (ρ) and $1/T$

thio)acetic acids were transformed into arylsulfinylacetic acids. Electron-releasing substituents speed up the oxidation process, while electron-withdrawing groups retard the rate. The Hammett's plot revealed that the ρ value is negative and decrease with increase in temperature. On the basis of experimental findings, structure-activity correlations were drawn. The proposed mechanism involves oxygen transfer from bromate to (phenylthio)acetic acid, resulting in the sulfoxide product. According to the experimental protocol, this reaction may be used to synthesize phenylsulfinylacetic acids in a selective manner.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- D.J. Pasto and R. Kent, *J. Org. Chem.*, **30**, 2684 (1965); <https://doi.org/10.1021/jo01019a042>
- K.S. Webb, *Tetrahedron Lett.*, **35**, 3457 (1994); [https://doi.org/10.1016/S0040-4039\(00\)73209-6](https://doi.org/10.1016/S0040-4039(00)73209-6)
- C. Srinivasan and K. Pitchumani, *Indian J. Chem.*, **17A**, 162 (1979).
- G. Panigrahi and R.N. Nayak, *Curr. Sci.*, **49**, 740 (1980).
- C. Srinivasan and K. Pitchumani, *Int. J. Chem. Kinet.*, **14**, 789 (1982); <https://doi.org/10.1002/kin.550140707>
- S. Kabilan, K. Pandiarajan, K. Krishnasamy and P. Sankar, *Int. J. Chem. Kinet.*, **27**, 443 (1995); <https://doi.org/10.1002/kin.550270504>
- C. Karunakaran, V. Ramachandran and P.N. Palanisamy, *Int. J. Chem. Kinet.*, **31**, 675 (1999); [https://doi.org/10.1002/\(SICI\)1097-4601\(1999\)31:9<675::AID-KIN8>3.0.CO;2-H](https://doi.org/10.1002/(SICI)1097-4601(1999)31:9<675::AID-KIN8>3.0.CO;2-H)
- N.M.I. Alhaj, A.M. Uduman Mohideen and S.S. Lawrence Mary, *E-J. Chem.*, **8**, 159 (2011); <https://doi.org/10.1155/2011/342409>
- N. Vijayalaxmi and E.V. Sundaram, *Indian J. Chem.*, **17A**, 495 (1979).
- S. Narayana and V.S. Srinivasan, *Indian J. Chem.*, **26A**, 110 (1987).
- K. Chipiso and R.H. Simoyi, *Aust. J. Chem.*, **69**, 1305 (2016); <https://doi.org/10.1071/CH16050>
- R.A. Adigun, M. Mhike, W. Mbiya, S.B. Jonnalagadda and R.H. Simoyi, *J. Phys. Chem. A*, **118**, 2196 (2014); <https://doi.org/10.1021/jp411790v>
- W. Mbiya, B. Choi, B.S. Martincigh, M.K. Morakinyo and R.H. Simoyi, *J. Phys. Chem. A*, **117**, 13059 (2013); <https://doi.org/10.1021/jp408304e>
- O. Olagunju and R.H. Simoyi, *J. Phys. Chem. A*, **12**, 6366 (2017); <https://doi.org/10.1021/acs.jpca.7b07587>
- Ch. Sanjeeva Reddy and E.V. Sundaram, *Tetrahedron*, **45**, 2109 (1989); [https://doi.org/10.1016/S0040-4020\(01\)80072-7](https://doi.org/10.1016/S0040-4020(01)80072-7)
- Ch. Sanjeeva Reddy and T. Vijayakumar, *Indian J. Chem.*, **35A**, 408 (1996).
- Ch. Sanjeeva Reddy and T. Vijayakumar, *Transition Met. Chem.*, **32**, 246 (2007); <https://doi.org/10.1007/s11243-006-0156-4>
- C.S. Reddy and P.S. Manjari, *J. Mol. Catal. Chem.*, **328**, 76 (2010); <https://doi.org/10.1016/j.molcata.2010.06.002>
- P.S. Manjari and C.S. Reddy, *Transition Met. Chem.*, **36**, 707 (2011); <https://doi.org/10.1007/s11243-011-9523-x>
- A. Chellamani and P. Sengu, *J. Mol. Catal. Chem.*, **283**, 83 (2008); <https://doi.org/10.1016/j.molcata.2007.12.004>
- K.B. Wiberg, *Physical Organic Chemistry*, Wiley: New York (1964).
- C.J. Collins and N.S. Bowman, *Isotopic Effects in Chemical Reactions*, Van Nostrand- Reinhold: New York (1970).
- L. Liu and Q.X. Guo, *Chem. Rev.*, **101**, 673 (2001); <https://doi.org/10.1021/cr990416z>
- P.K. Sharma, *Asian J. Chem.*, **26**, 2702 (2014); <https://doi.org/10.14233/ajchem.2014.16081>
- A. Indelli, G. Nolan Jr. and E.S. Amis, *J. Am. Chem. Soc.*, **82**, 3233 (1960); <https://doi.org/10.1021/ja01498a001>
- M. Anbar and S. Guttman, *J. Am. Chem. Soc.*, **83**, 4741 (1961); <https://doi.org/10.1021/ja01484a013>
- C.A. Wright and A.F.M. Barton, *J. Chem. Soc. A*, 1747 (1968); <https://doi.org/10.1039/J19680001747>
- G. Rábai, G. Bazsa and M.T. Beck, *Int. J. Chem. Kinet.*, **13**, 1277 (1981); <https://doi.org/10.1002/kin.550131207>
- D.G. Lee and T. Chen, *J. Org. Chem.*, **56**, 5346 (1991); <https://doi.org/10.1021/jo00018a026>
- A. Chellamani, N. Ismail Alhaji, S. Rajagopal, R. Sevvell and C. Srinivasan, *Tetrahedron*, **51**, 12677 (1995); [https://doi.org/10.1016/0040-4020\(95\)00825-S](https://doi.org/10.1016/0040-4020(95)00825-S)
- Y. Goto, T. Matsui, S. Ozaki, Y. Watanabe and S. Fukuzumi, *J. Am. Chem. Soc.*, **121**, 9497 (1999); <https://doi.org/10.1021/ja9901359>
- E.S. Lewis, *Investigation of Rates and Mechanisms of Reactions*, Wiley: New York, Eds.: 3, p. 415 (1974)
- O. Exner, *Chem. Commun.*, **17**, 1655 (2000); <https://doi.org/10.1039/b002758h>
- O. Exner, *Collect. Czech. Chem. Commun.*, **29**, 1094 (1964); <https://doi.org/10.1135/cccc19641094>
- F. Ruff and A.J. Kucsmán, *J. Chem. Soc., Perkin Trans. II*, **5**, 683 (1985); <https://doi.org/10.1039/p29850000683>
- K. Nagajyothi, P.S. Raghavan and R. Gopalan, *Asian J. Chem.*, **22**, 839 (2010).