



Kinetics and mechanism of peroxy sulfate/ NaNO_2 mediated nitration of phenols in aqueous bisulfate medium

Muppidi Suresh^{1,2} · K. C. Rajanna^{1,3} · Y. Hemanth Sriram¹ · Y. Rajeshwer Rao³

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Abstract

Peroxy sulfates (PS) like peroxydisulfate (PDS), and peroxy monosulfate (PMS) have been accomplished as an efficient reagents for $\text{KHSO}_4/\text{NaNO}_2$ mediated nitration of aromatic compounds (S) such as phenols in aqueous bisulfate and acetonitrile medium, under the conditions $[\text{NaNO}_2] \gg [\text{PS}]$. The kinetics of the reaction depicted first order dependence on [S], $[\text{NaNO}_2]$, and [PS]. Reaction rates were sensitive to the introduction of electron donating or withdrawing groups. However, our efforts to correlate the kinetic results into Hammett's structure–reactivity equation were not fruitful. Observed deviations from the linearity of Hammett's equation have been interpreted in terms of effective Hammett's constants ($\bar{\sigma}$ or σ_{eff}), para resonance interaction energy ($\Delta\Delta G_p$) values and Yukawa–Tsuno's resonance stabilization parameter (r). The observed negative magnitude of entropy of activation (ΔS^\ddagger) values suggests greater solvation and/or cyclic transition state before yielding products.

Keywords Peroxy sulfates (PS) · Peroxydisulfate (PDS) · Peroxy monosulfate (PMS) · $\text{KHSO}_4/\text{NaNO}_2$ mediated nitration · Aromatic compounds · Structure–reactivity study

1 Introduction

Peroxy sulfur salts (PS) like peroxydisulfate (PDS) and peroxy monosulfate (PMS) are among the family of the most versatile oxidants in aqueous solution [1–15]. The peroxydisulfate ion ($\text{S}_2\text{O}_8^{2-}$), and the peroxy monosulfate ion (SO_5^{2-}) are oxyanions. Both PDS and PMS are powerful oxidizing agents with reduction potentials (PDS with $E^\circ = 2.01$ V, and PMS with $E^\circ = 1.84$ V) higher than H_2O_2 ($E^\circ = 1.76$ V) [2]. Important salts comprising peroxydisulfate (PDS) anion include sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$). These salts are colourless, water-soluble solids, which are available easily at a low cost and affordable to any laboratory as bench top chemicals. These salts are

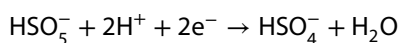
highly stable at ambient temperatures with ease of storage and transport [2]. The use of persulfate has recently been the focus of attention for an alternative oxidant in the chemical oxidation of contaminants [5–9]. Review articles published by House [1], Wilmarth and Haim [2] furnish excellent bibliography and summary of the results pertain to the kinetic studies and their plausible mechanisms prior to 1961. On the other hand, Potassium peroxy monosulfate (potassium monopersulfate, Caroat, Oxone or PMS) is well known for the oxidation of boron-, nitrogen-, phosphorus-, and sulfur-containing compounds [10–24]. In highly acidic solutions the standard electrode potential for this compound is +2.51 V with a half reaction generating the hydrogen sulfate ($\text{pH}=0$), which makes it as effective oxidizing agent [23].

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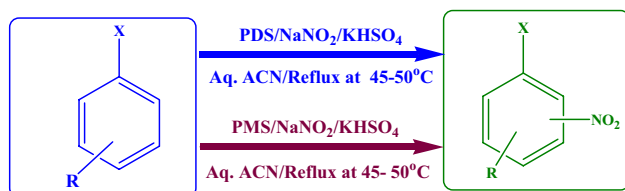


Nitration of aromatic and heteroaromatic compounds has received a surging impact because nitroarenes are widely used as important intermediates and precursors during the synthesis of organic and organometallic compounds, pharmaceuticals, explosives, dyes, polymers, pesticides, plastics, drugs and medicines [25–28]. The classical mixed acid or acid mixture (mixture of two strong acids, sulfuric and nitric acid) method of nitration is still used in industries, which is a notoriously polluting process because it generates large quantities of hazardous waste acid streams. But in the past several decades, several alternative synthetic protocols were used to prevent such acid waste [25–28]. In this part of the work the authors have taken up the kinetics and mechanism of PDS and PMS triggered nitration of aromatic compounds with a hope that the findings will contribute to the greenery of nitration reactions because the reagents such as PDS, sodium nitrite, and bisulphate used herein are green chemicals and the excess outlets are minimum under kinetic conditions (Scheme 1).

2 Experimental details

2.1 General

Reagent grade chemicals procured from Avra, Loba, Merck, SD fine chemicals, which are used as such without further purification. Distilled water purified over acid dichromate and alkaline permanganate is used for preparation of solutions. HPLC grade acetonitrile is used to prepare stock solutions of phenolic compounds. Systronics Model 144 spectrophotometer was used to follow the increase in absorbance of the nitro product (OD or Absorbance(A)) at 400 nm.



Scheme 1 Peroxysulfates/ NaNO_2 mediated nitration of aromatic compounds in aqueous bisulfate medium

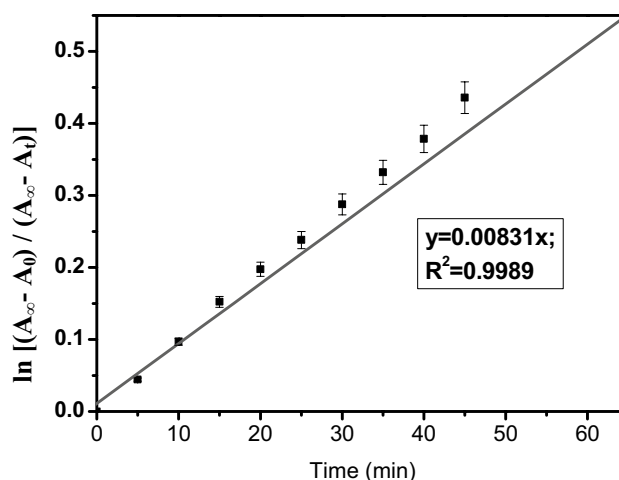


Fig. 1 First order plot of phenol. $10^3[\text{Phenol}] = 5.0 \text{ mol/dm}^3$; $10^4[\text{PDS}] = 5.0 \text{ mol/dm}^3$; $10^3[\text{NaNO}_2] = 5.0 \text{ mol/dm}^3$; $10^3[\text{KHSO}_4] = 5.0 \text{ mol/dm}^3$; $\text{MeCN}(\% \text{ V/V}) = 5.0$; temperature = 313 K

2.2 Kinetic method of following the reaction

The reactant solutions were kept stirred in a water thermostat at desired temperature, and, samples were pipetted out into a cuvette at different time intervals, and the coloured product analysed spectrophotometrically. Systronics Model 144 spectrophotometer was used to follow the increase in absorbance of the compound (OD or A) at 405 nm. Absorbance values were in agreement with each other with an accuracy of ± 3 percentage error. The kinetic runs were conducted under pseudo order conditions $[\text{Phenol}]$ and $[\text{NaNO}_2] \gg [\text{catalyst}]$ ([PDS] or [PMS]) in aqueous KHSO_4 solutions. We have used graphical method of approach to determine order of reaction using the following first order and second order rate Eqs. (1 and 2) appropriately depending on reaction conditions.

$$\ln[(A_\infty - A_0)/(A_\infty - A_t)] = k't \quad (1)$$

$$\frac{1}{(A_\infty - A_t)} = kt + \frac{1}{(A_\infty - A_0)} \quad (2)$$

In the above expressions, if (x) is the product obtained during the course of reaction, and (a) the initial concentration of reactant, (a-x) represents unreacted concentration of reactant at given instant of time (t). If A_t is the absorbance of nitrate species produced during the course of reaction at a given time, A_∞ is the absorbance at infinite time (at the end of the reaction) and A_0 , the absorbance (if any) before the on-take of reaction, then $(A_\infty - A_0)$ and $(A_\infty - A_t)$ are proportional to (a) and (a-x) respectively. The pseudo first-order logarithmic plots $[\ln(A_\infty - A_0)/(A_\infty - A_t)]$

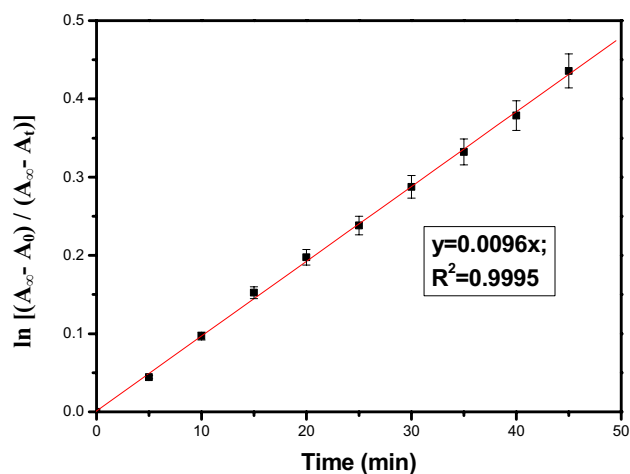


Fig. 2 First order plot of *P*-Cresol. 10^3 [*P*-Cresol]=5.0 mol/dm³; 10^4 [PDS]=5.0 mol/dm³; 10^3 [NaNO₂]=5.0 mol/dm³; 10^3 [KHSO₄]=5.0 mol/dm³; MeCN(% V/V)=5.0; temperature = 298 K

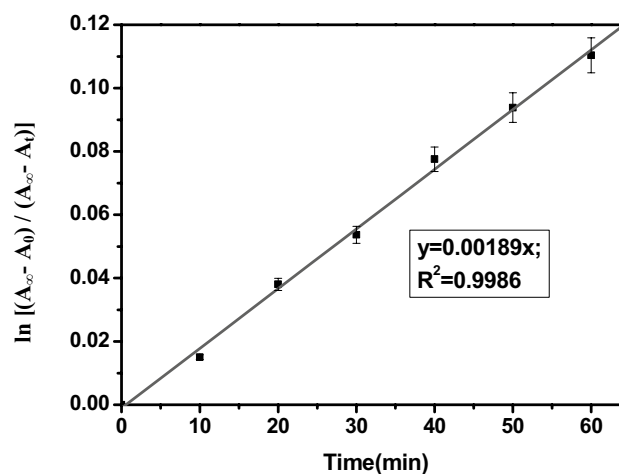


Fig. 4 First order plot of phenol. 10^3 [Phenol]=5.0 mol/dm³; 10^4 [PMS]=5.0 mol/dm³; 10^3 [NaNO₂]=5.0 mol/dm³; 10^3 [KHSO₄]=0.010 mol/dm³; MeCN(% V/V)=5.0; temperature = 303 K

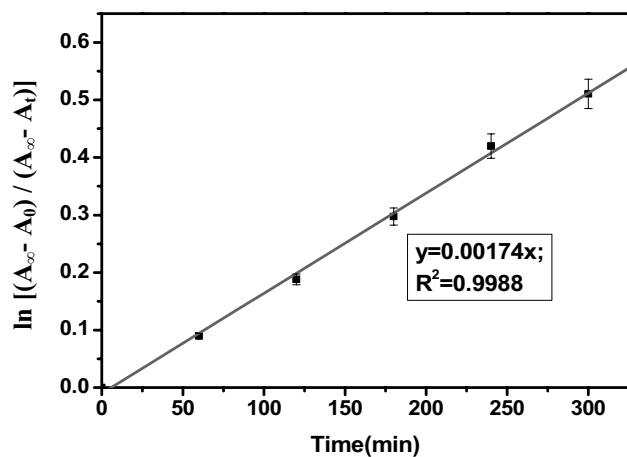


Fig. 3 First order plot of *P*-Chloro phenol. 10^3 [*P*-Chloro phenol]=5.0 mol/dm³; 10^4 [PDS]=5.0 mol/dm³; 10^3 [NaNO₂]=5.0 mol/dm³; 10^3 [KHSO₄]=5.0 mol/dm³; MeCN(% V/V)=5.0; temperature = 298 K

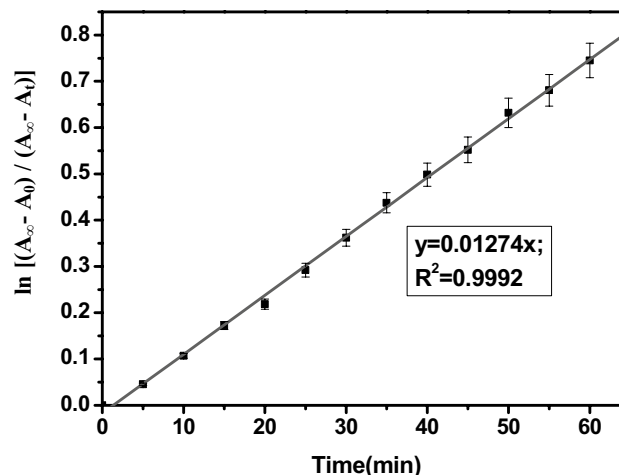


Fig. 5 First order plot of *P*-Cresol. 10^3 [*P*-Cresol]=5.0 mol/dm³; 10^4 [PMS]=5.0 mol/dm³; 10^3 [NaNO₂]=5.0 mol/dm³; 10^3 [KHSO₄]=0.010 mol/dm³; MeCN(% V/V)=5.0; temperature = 308 K

versus time were linear passing through origin indicating first order kinetics in [Peroxyulfate] ([PDS] and [PMS]), as shown in Figs. 1, 2, 3, 4, 5 and 6. The observed first-order rate constants, k' , were evaluated from the slopes of these plots. The plot of (k') versus [Substrate] was linear, passing through the origin (under otherwise similar conditions) showing first order dependence on [Substrate] (Figs. 7, 8). The plot of $(1/(A_{\infty} - A_t))$ versus time under pseudo second order conditions $[\text{NaNO}_2] \gg [\text{Catalyst}] = [\text{Phenol}], [\text{KHSO}_4]$ (where A_0 , A_t and A_{∞} are the absorbance at any given time t and at the end of the reaction respectively). Representative second order plots are given in Figs. 9, 10, 11, 12 and 13 respectively.

2.3 General procedure for synthesis of nitroarenes under kinetic conditions

We have taken up the synthesis of nitroarenes under kinetic conditions used in the present study to identify and confirm the reaction products. Reaction mixture prepared under kinetic conditions in a clean two necked round bottom flask and constantly stirred the mixture under reflux conditions. Progress of the reaction was monitored chromatographically with TLC. After completion, the reaction mixture was treated with NaHCO₃ solution to attain neutral conditions. The organic layer was separated, dried

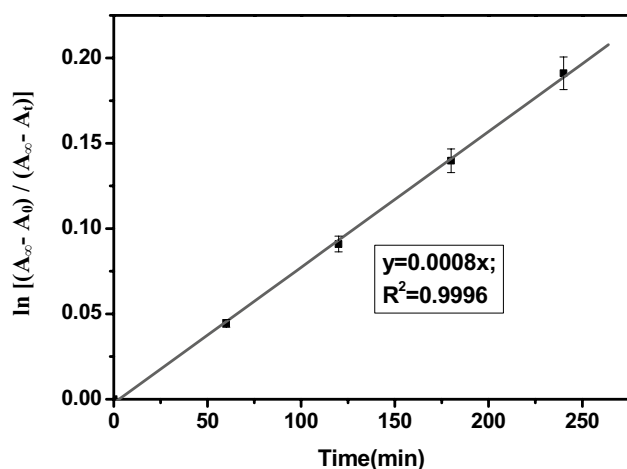


Fig. 6 First order plot of *P*-chloro Phenol. 10^3 [*P*-chloro Phenol] = 5.0 mol/dm³; 10^4 [PMS] = 5.0 mol/dm³; 10^3 [NaNO₂] = 5.0 mol/dm³; 10^3 [KHSO₄] = 0.010 mol/dm³; MeCN(% V/V) = 5.0; temperature = 303 K

over Na₂SO₄ and evaporated under vacuum. The crude product was purified by column chromatography using ethyl acetate – hexane as eluent to get pure product. The

synthesized compounds were characterized by ¹H NMR and mass spectroscopic methods (Table 1).

2.4 Test for the detection of free radicals

Freshly prepared acrylamide or deaerated acrylonitrile were added to the reaction mixture containing potassium peroxydisulfate (PDS) and/or peroxymonosulfate (PMS) under nitrogen atmosphere in situ in order to detect the formation of free radical intermediates during the course of reaction, olefinic monomers to detect whether free radical intermediates are formed in situ during the course of reaction. Peroxysulfates such as potassium peroxydisulfate (PDS) and/or peroxymonosulfate (PMS) did not initiate/induce polymerization of added olefinic monomers even after 24 h under reflux conditions. This observation indicated the absence of free radical intermediates during the course of present reaction.

2.5 Effect of variation of [additives]

In order to have a closer look into the mechanism and the rate law, effect of variation of different additives like [KHSO₄]

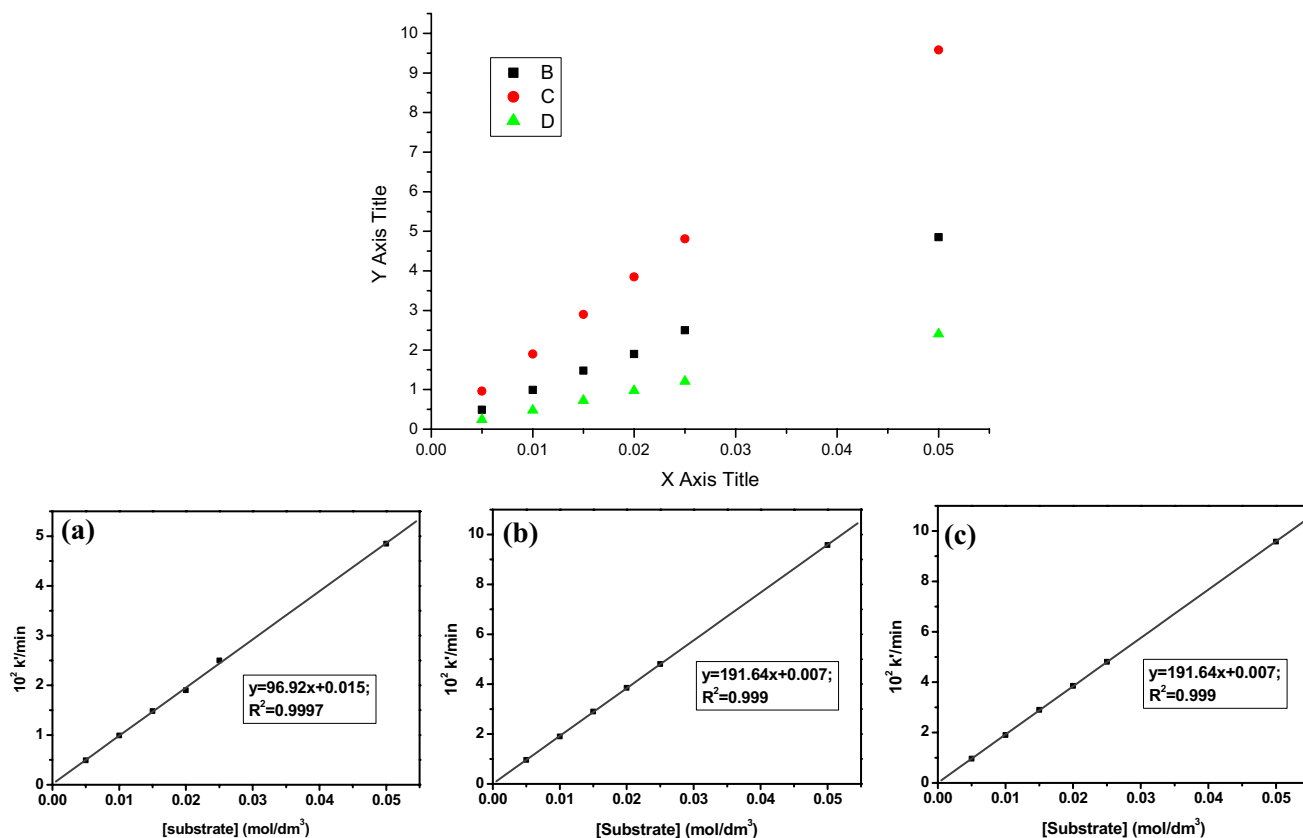


Fig. 7 Plots of (k') versus [Sub] in PDS/NaNO₂ mediated nitration reactions of Phenols. 10^4 [PDS] = 5.0 mol/dm³; 10^3 [NaNO₂] = 5.0 mol/dm³; 10^3 [KHSO₄] = 0.010 mol/dm³; MeCN(% V/V) = 5.0; temperature = 298 K; **a** Phenol, **b** p-Cresol, **c** p-Bromophenol

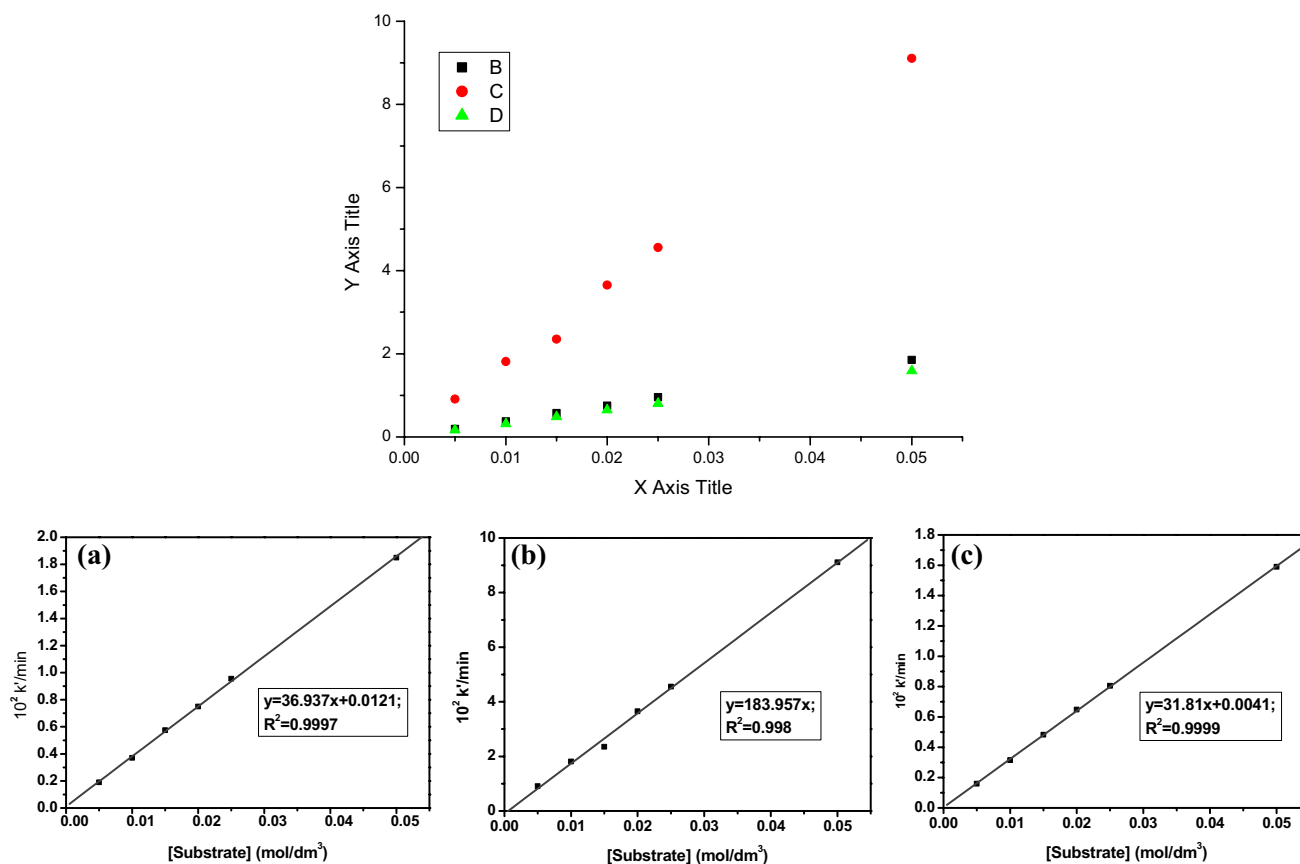


Fig. 8 Plots of (k') versus $[\text{Sub}]$ in PMS/ NaNO_2 mediated nitration reactions of Phenols. $10^4[\text{PMS}]=5.0 \text{ mol/dm}^3$; $10^3[\text{NaNO}_2]=5.0 \text{ mol/dm}^3$; $10^3[\text{KHSO}_4]=0.010 \text{ mol/dm}^3$; $\text{MeCN}(\% \text{ V/V})=5.0$; temperature = 298 K; **a** Phenol, **b** P-Cresol, **c** p-Bromophenol

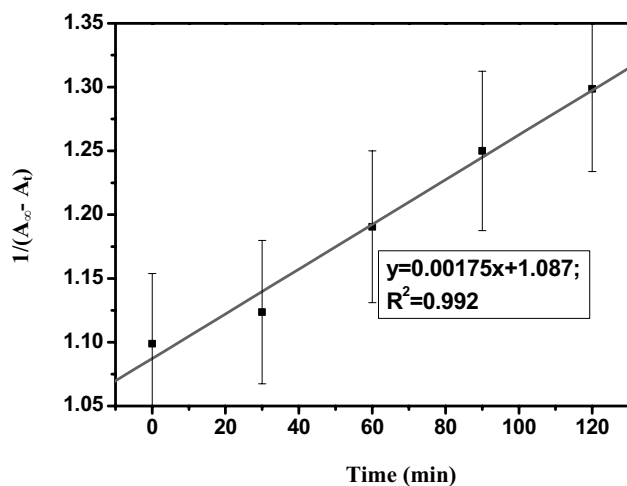


Fig. 9 Second order plot of phenol. $10^4[\text{Phenol}]=5.0 \text{ mol/dm}^3$; $10^4[\text{PDS}]=5.0 \text{ mol/dm}^3$; $10^3[\text{NaNO}_2]=5.0 \text{ mol/dm}^3$; $10^3[\text{KHSO}_4]=5.0 \text{ mol/dm}^3$; $\text{MeCN}(\% \text{ V/V})=5.0$; temperature = 298 K

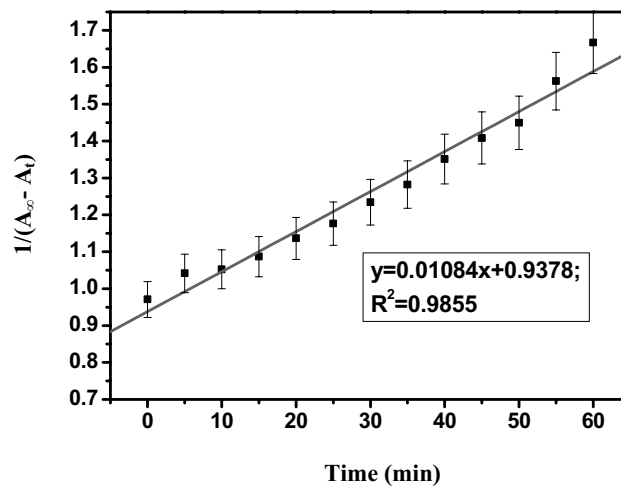


Fig. 10 Second order plot of P-Cresol. $10^4[\text{P-Cresol}]=5.0 \text{ mol/dm}^3$; $10^4[\text{PDS}]=5.0 \text{ mol/dm}^3$; $10^3[\text{NaNO}_2]=5.0 \text{ mol/dm}^3$; $10^3[\text{KHSO}_4]=5.0 \text{ mol/dm}^3$; $\text{MeCN}(\% \text{ V/V})=5.0$; temperature = 298 K

(0.005–0.050 mol/dm³), $[\text{NaNO}_2]$ (0.001–0.010 mol/dm³), and $[\text{peroxysulfate}]$ (0.001–0.002 mol/dm³) were studied under otherwise similar conditions (Table 2). None of these

additives had any significant effect on the the rate of nitration. These observations put together probably point out that peroxy sulphates (PDS and/or PMS) are stoichiometric

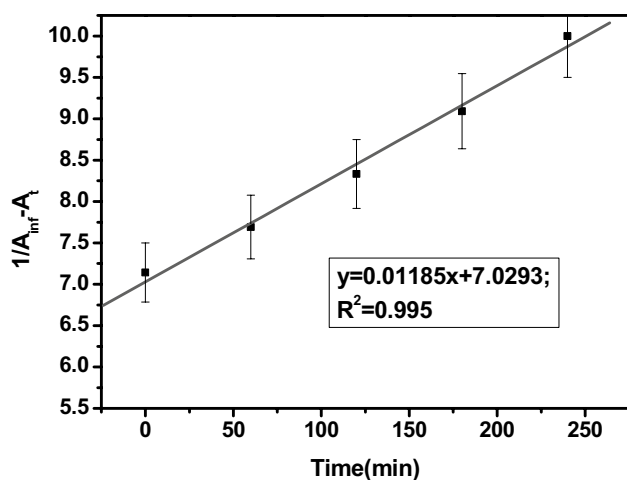


Fig. 11 Second order plot for *P-chloro* Phenol. 10^4 [*P-chloro* Phenol]=5.0 mol/dm³; 10^4 [PDS]=5.0 mol/dm³; 10^3 [NaNO₂]=5.0 mol/dm³; 10^3 [KHSO₄]=5.0 mol/dm³; MeCN(% V/V)=5.0; temperature=298 K

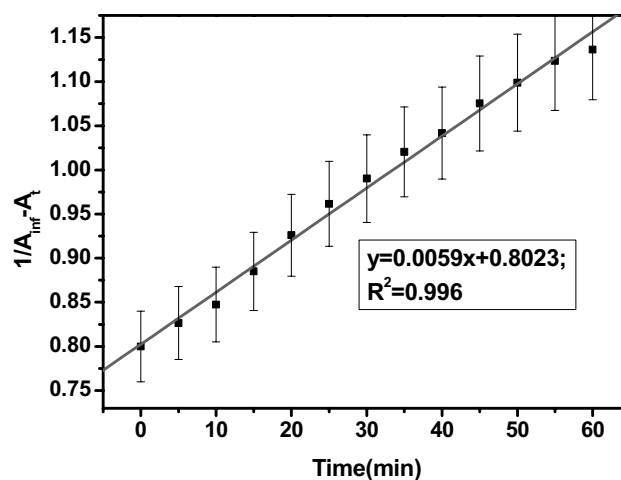


Fig. 13 Second order plot of *P-Cresol*. 10^4 [*P-Cresol*]=5.0 mol/dm³; 10^4 [PMS]=5.0 mol/dm³; 10^3 [NaNO₂]=5.0 mol/dm³; 10^3 [KHSO₄]=5.0 mol/dm³; MeCN(% V/V)=5.0; temperature=298 K

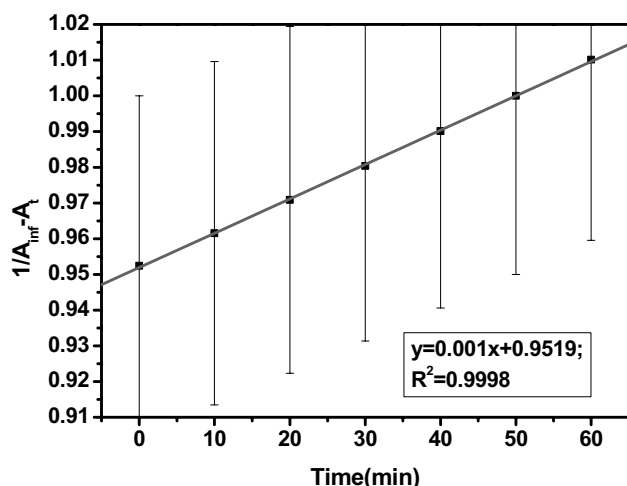


Fig. 12 Second order plot of phenol. 10^4 [Phenol]=5.0 mol/dm³; 10^4 [PMS]=5.0 mol/dm³; 10^3 [NaNO₂]=5.0 mol/dm³; 10^3 [KHSO₄]=5.0 mol/dm³; MeCN(% V/V)=5.0; temperature=298 K

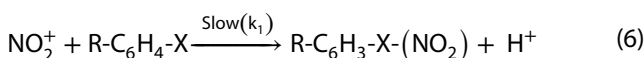
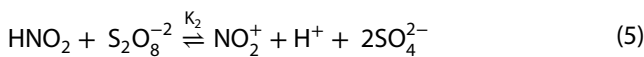
reagents, which in situ generate nitronium ion species when they react with nitrite (NO₂⁻) in the presence of mild acid (obtained from the dissociation of (HSO₄⁻) bisulphate anion). Further, the constancy in the *k'*-values with the increase in [PS] confirms that order with respect to [PS] is unity.

3 Results and discussion

3.1 Reactive species and mechanism of nitration in PDS/NaNO₂ mediated nitration of aromatic compounds

Persulfate is known to exist mainly as PDS anion (S₂O₈²⁻) in aqueous solution. However, in the present study, nitration

of aromatic compounds is conducted in presence of NaNO₂ by taking [NaNO₂] ≫ [PDS] in aqueous bisulphate (HSO₄⁻) medium. Nitrite picks up a proton, released from the dissociation of HSO₄⁻ to form (HNO₂), which could be oxidised PDS anion (S₂O₈²⁻) to generate active nitronium ion (NO₂⁺), as reported by Edwards and coworkers [8]. Nitronium ion thus formed, reacts with aromatic compounds (R-C₆H₄-X) in a slow step undergo electrophilic nitration to afford the nitro aromatic compounds, according to the following reaction steps:



Rate-law for the above sequence of mechanistic steps could be derived as given in the following steps using equilibria (3–5) and step (4).

$$\text{Rate} = -d[\text{R-C}_6\text{H}_4\text{-X}]/dt = k_1 [\text{NO}_2^+][\text{R-C}_6\text{H}_4\text{-X}] \quad (7)$$

From step (3)

$$[\text{NO}_2^+] = K_2 [\text{HNO}_2] [\text{S}_2\text{O}_8^{2-}] / [\text{SO}_4^{2-}]^2 \quad (8)$$

But from step (4) in situ produced [HNO₂] could be evaluated as,

Table 1 Peroxydisulphate (PDS) and peroxymonosulphate (PMS) as catalysts for nitration of Phenols

Entry	Substrate	Product	PDS		PMS	
			R.T (h)	Yield (%)	R.T (h)	Yield (%)
1	Phenol	2-NO ₂ phenol	2	70	4	70
2	<i>o</i> -Cresol	2-Me- 4-NO ₂ phenol	2	70	4	68
3	<i>P</i> -Cresol	2-NO ₂ 4-Me phenol	2	75	4	74
4	<i>m</i> -Cresol	3-Me- 4-NO ₂ phenol	2	70	4	68
5	<i>o</i> -Cl phenol	4-NO ₂ 2-Cl phenol	4	80	6	80
6	<i>m</i> -Cl phenol	4-NO ₂ 3-Cl phenol	4	78	6	78
7	<i>p</i> -Cl phenol	2-NO ₂ 4-Cl phenol	4	80	6	80
8	<i>p</i> -Br phenol	2-NO ₂ 4-Br phenol	4	75	6	77
9	<i>o</i> -OH phenol	4- NO ₂ benzene-1,2-diol	3	85	4	80
10	<i>m</i> -OH phenol	4- NO ₂ benzene-1,3-diol	3	80	4	77
11	<i>p</i> -OH phenol	2- NO ₂ benzene-1,4-diol	3	80	4	80
12	<i>p</i> -Nitro phenol	2,4- <i>di</i> Nitro phenol	4	75	6	75
13	<i>p</i> -Amino phenol	2-Nitro4-Amino phenol	3	80	6	80
14	α -Naphthol	2- NO ₂ -1-Naphthol	2	85	4	80
15	β -Naphthol	1-NO ₂ -2-Naphthol	3	85	5	80

$$[\text{HNO}_2] = K_1[\text{NO}_2^-][\text{H}^+] \quad (9)$$

Substituting for $[\text{HNO}_2]$ from Eq. (9) into Eq. (8), $[\text{NO}_2^+]$ could be obtained as,

$$[\text{NO}_2^+] = K_1 K_2 [\text{S}_2\text{O}_8^{2-}] [\text{NO}_2^-] [\text{H}^+] / [\text{SO}_4^{2-}]^2 \quad (10)$$

From step (3), $[\text{H}^+]$ can be obtained from the dissociation step of (HSO_4^-) as,

$$[\text{H}^+] = (K_d[\text{HSO}_4^-] / [\text{SO}_4^{2-}]) \quad (11)$$

Substitution of $[\text{H}^+]$ from Eq. (11) into Eq. (10), $[\text{NO}_2^+]$ could be again reduced to,

$$[\text{NO}_2^+] = K_d K_1 K_2 [\text{PDS}] [\text{HSO}_4^-] [\text{NO}_2^-] / [\text{SO}_4^{2-}]^3 \quad (12)$$

(where PDS = $\text{S}_2\text{O}_8^{2-}$)

Now, substitution of active species $[\text{NO}_2^+]$ from Eq. (12) into Eq. (7), final rate law comes out as,

$$\begin{aligned} \text{Rate} &= -d[\text{R}-\text{C}_6\text{H}_4-\text{X}]/dt \\ &= kK_d K_1 K_2 [\text{PDS}] \frac{[\text{HSO}_4^-] [\text{NO}_2^-] [\text{R}-\text{C}_6\text{H}_4-\text{X}]}{[\text{SO}_4^{2-}]^3} \quad (13) \end{aligned}$$

Above rate equation is in consonance with the observed kinetic results viz., first order in [Substrate] (i.e., $\text{R}-\text{C}_6\text{H}_4-\text{X}$), and [PDS]. Since $[\text{NO}_2^-]$ is taken in large excess over [PDS], and $[\text{KHSO}_4]$, it implies that order in [active NO_2^+ species] is also one. Bisulphate term ($[\text{HSO}_4^-]$) appeared in the

Table 2 Effect of variation of [Additives] on pseudo first order rate constants (k') in PDS, PMS (PS)/ NaNO_2 mediated nitration reactions of phenol

10^4 [PS] (mol/dm ³)	10^3 [NaNO_2] (mol/dm ³)	[KHSO_4] (mol/dm ³)	10^3 k'/min	
			PDS	PMS
5.00	5.00	0.005	4.90	1.90
5.00	5.00	0.010	4.85	1.82
5.00	5.00	0.015	4.80	1.99
5.00	5.00	0.020	4.94	1.78
5.00	5.00	0.025	4.79	1.80
5.00	5.00	0.050	4.95	1.95
5.00	1.00	0.010	4.81	1.79
5.00	2.00	0.010	4.98	1.93
5.00	4.00	0.010	5.00	2.00
5.00	8.00	0.010	5.05	1.85
5.00	10.0	0.010	4.92	1.96
10.0	20.0	0.010	4.99	1.87
15.0	20.0	0.010	5.10	1.97
20.0	20.0	0.010	4.82	2.05

10^3 [Phenol] = 5.0 mol/dm³; MeCN(% V/V) = 5.0; temperature = 303 K

numerator of rate law is negated by ($[\text{SO}_4^{2-}]^3$) term in the denominator, thus accounting for the observed negligible (HSO_4^-) effect on rate of the reaction. Thus, at constant (HSO_4^-) concentration, and known excess of $[\text{NO}_2^-]$ the rate law reduces to,

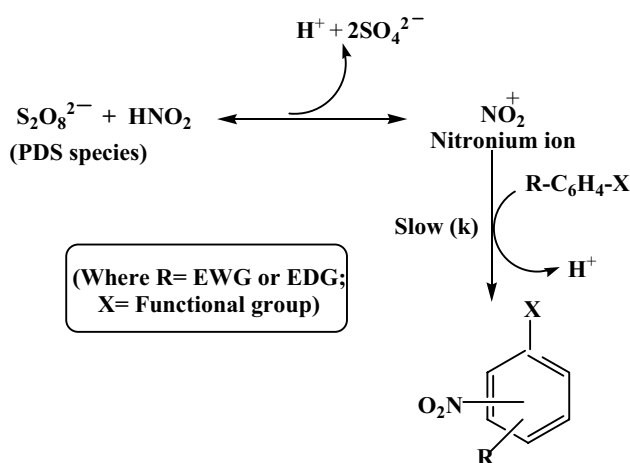
$$\text{Rate} = -d[\text{R-C}_6\text{H}_4\text{-X}]/dt = k[\text{NO}_2^+][\text{R-C}_6\text{H}_4\text{-X}]$$

$$\left(\text{where } [\text{NO}_2^+] = \left(K_d K_1 K_2 [\text{PDS}][\text{HSO}_4^-][\text{NO}_2^-]/[\text{SO}_4^{2-}]^3\right)\right)$$
(14)

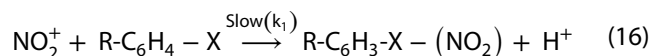
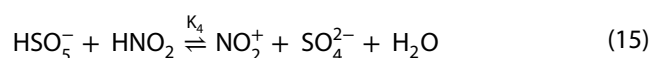
On the basis of the foregoing discussion, the sequential mechanistic steps for the nitration of aromatic compounds of this study can be summarized as shown in Scheme 2.

3.2 Reactive species and mechanism of nitration in PMS/NaNO₂ mediated nitration of aromatic compounds

Potassium Permonosulfate is a salt of Caro's acid (H₂SO₅), which is known to mainly exist as PMS (HSO₅⁻). Present investigation (the nitration reactions) is taken up in aqueous bisulphate (HSO₄⁻) solutions, under the conditions [NaNO₂] ≫ [PMS], [HSO₄⁻]; [HSO₄⁻] > [PMS]. Bisulphate (HSO₄⁻) behaves like a monoprotic acid and gives a proton (H⁺) according to the equilibrium (1) as mentioned in the previous section. In aqueous HSO₄⁻ medium Nitrite ion (NO₂⁻) may protonate to form HNO₂. The PMS (HSO₅²⁻) may oxidize HNO₂ and generate active nitronium ion (NO₂⁺) species in situ, which in turn reacts with aromatic compounds (R-C₆H₄-X) in a slow step, which undergo electrophilic nitration and afford the nitro aromatic compounds, as shown in the following reaction steps, given in the following steps



Scheme 2 PDS/NaNO₂ mediated mechanism of Nitration of aromatic compounds



Rate-law for these mechanistic steps could be derived using equilibria (3, 4 and 1) and step (1).

$$\text{Rate} = -d[\text{R-C}_6\text{H}_4\text{-X}]/dt = k_1 [\text{NO}_2^+][\text{R-C}_6\text{H}_4\text{-X}] \quad (17)$$

From step (1)

$$[\text{NO}_2^+] = K_4 [\text{HSO}_5^-][\text{HNO}_2]/[\text{SO}_4^{2-}] \quad (18)$$

But from step (4) in situ produced [HNO₂] could be evaluated as,

$$[\text{HNO}_2] = K_1 [\text{H}^+][\text{NO}_2^-] \quad (19)$$

Substituting for [HNO₂] from Eq. (19) into Eq. (18), [NO₂⁺] could be given as,

$$[\text{NO}_2^+] = K_1 K_4 [\text{HSO}_5^-][\text{NO}_2^-][\text{H}^+]/[\text{SO}_4^{2-}] \quad (20)$$

Upon substitution of [H⁺] from Eq. (11) into Eq. (18) and further simplification, the active species [NO₂⁺] could be written as,

$$[\text{NO}_2^+] = K_d K_1 K_4 [\text{HSO}_5^-][\text{NO}_2^-][\text{HSO}_4^-]/[\text{SO}_4^{2-}]^2 \quad (21)$$

Substitution of active species [NO₂⁺] from Eq. (21) into Eq. (19), final rate law comes out as,

$$\text{Rate} = -d[\text{R-C}_6\text{H}_4\text{-X}]/dt$$

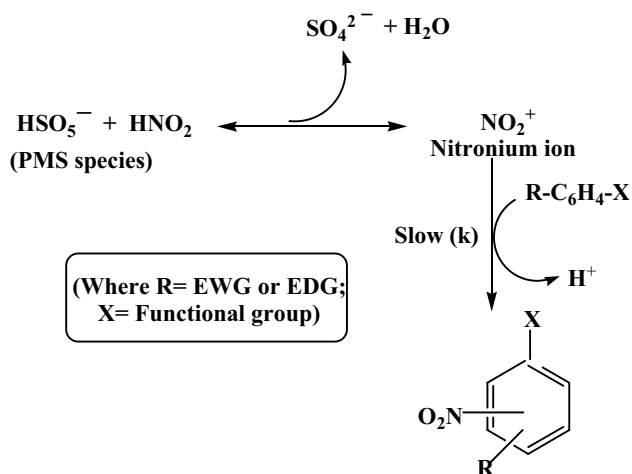
$$= (kK_d K_1 K_4 [\text{HSO}_5^-][\text{NO}_2^-][\text{HSO}_4^-][\text{R-C}_6\text{H}_4\text{-X}])/[\text{SO}_4^{2-}]^2$$

Above rate equation is keeping in with the observed kinetic results viz., first order in [Substrate] (i.e., R-C₆H₄-X), and [PMS]_t. Since [NO₂⁻]_t ≫ [PMS]_t, and [KHSO₄], it is understood that order in [active NO₂⁺ species] is also one. Bisulphate term ([HSO₄⁻]) appeared in the numerator of the rate law is negated by (SO₄²⁻) term in the denominator, suggesting the observed negligible (HSO₄⁻) effect on rate of the reaction. Thus, at constant (HSO₄⁻) concentration, and known excess that rate law reduces to,

$$\text{Rate} = -d[\text{R-C}_6\text{H}_4\text{-X}]/dt = k[\text{NO}_2^+][\text{R-C}_6\text{H}_4\text{-X}]$$

$$\left(\text{where, } [\text{NO}_2^+] = K_d K_1 K_4 [\text{HSO}_5^-][\text{NO}_2^-][\text{HSO}_4^-]/[\text{SO}_4^{2-}]^2\right)$$

On the basis of the foregoing discussion, the sequential mechanistic steps for the nitration of aromatic compounds of this study can be summarized as shown in Scheme 3.



Scheme 3 PMS/NaNO₂ mediated mechanism of nitration of aromatic compounds

3.3 Temperature effect on the rate of nitration

The PDS and PMS catalysed nitration of different phenols reactions have been studied in different aqueous acetonitrile medium at four to five temperatures in twenty centigrade degree range (300–325°K). The free energy of activation (ΔG^\ddagger) at a given temperature is calculated using Eyring's theory of reaction rates [29, 30] using the following steps:

$$\Delta G^\ddagger = RT \ln(RT/Nhk)$$

Substituting for R, N, and h (in SI units), ΔG^\ddagger could be simplified accordingly as,

$$\Delta G^\ddagger = 8.314 \times T[23.7641 + \ln(T/k)]$$

Substituting the value of a temperature (T) in Kelvin degrees and second order rate constant (k), ΔG^\ddagger could be obtained. We have also evaluated enthalpy and entropies of activation (ΔH^\ddagger and ΔS^\ddagger) from the slope and intercept values of the Gibbs-Helmholtz plot ΔG^\ddagger versus temperature (T), according to the following relationship:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Few representative Gibbs-Helmholtz plots for PDS and PMS catalytic nitration reactions are given in Figs. 14, 15, 16, 17, 18 and 19. Activation parameters thus evaluated are compiled in Table 3.

3.4 Quantitative structure and reactivity study

A perusal of the kinetic revealed that the introduction of electron donating or withdrawing groups (EDG and EWG) into the aromatic ring generally altered the rate of

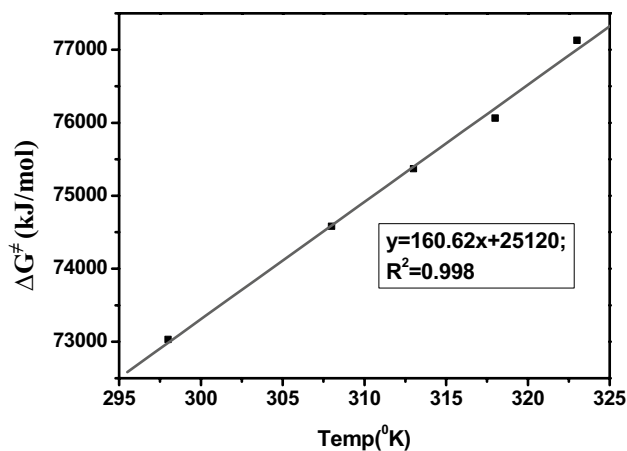


Fig. 14 Gibbs-Helmholtz plot (ΔG^\ddagger vs temperature) for PDS/NaNO₂ mediated nitration of phenol

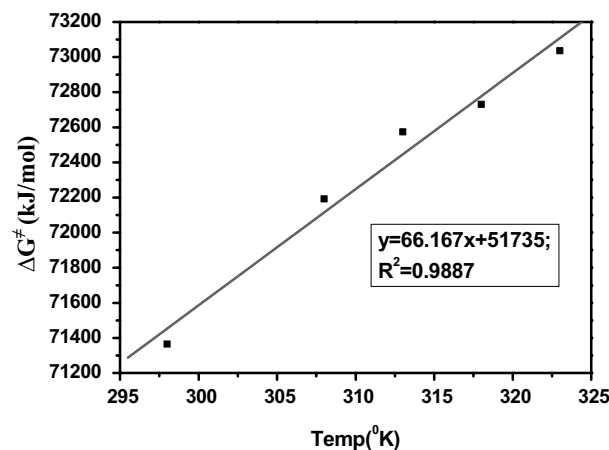


Fig. 15 Gibbs-Helmholtz plot (ΔG^\ddagger vs temperature) for PDS/NaNO₂ mediated nitration of p-Cresol

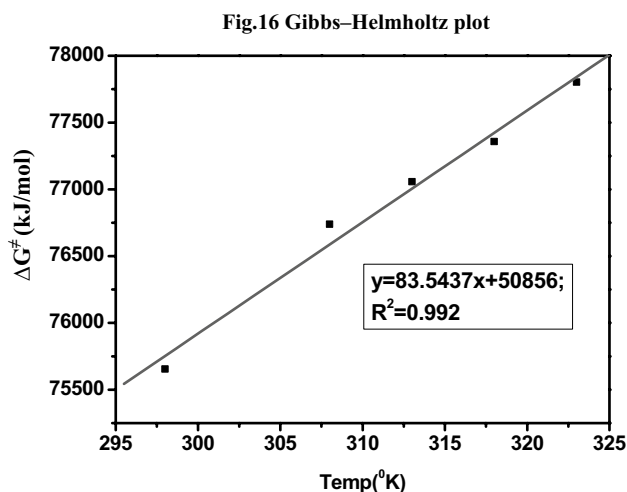


Fig. 16 Gibbs-Helmholtz plot (ΔG^\ddagger vs temperature) for PDS/NaNO₂ mediated nitration of P-chloro phenol

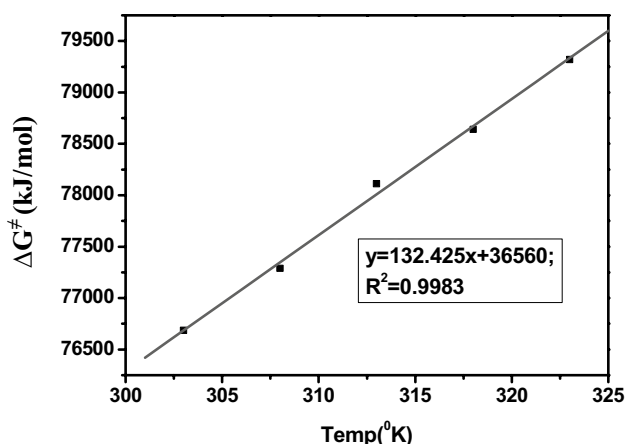


Fig. 17 Gibbs-Helmholtz plot (ΔG^\ddagger vs temperature) for PMS/ NaNO_2 mediated nitration of phenol

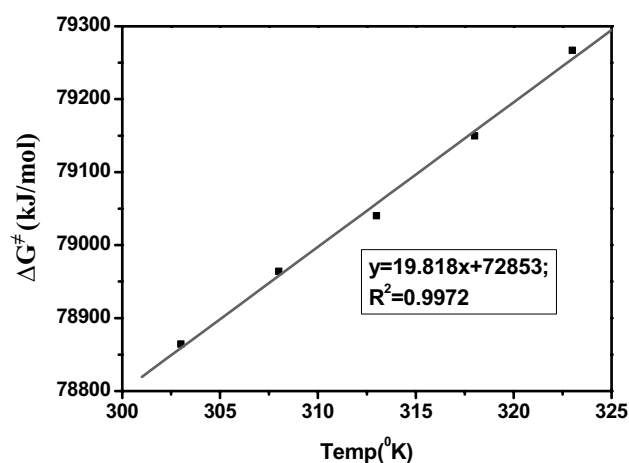


Fig. 19 Gibbs-Helmholtz plot (ΔG^\ddagger vs temperature) for PMS/ NaNO_2 mediated nitration of *P-chloro* phenol

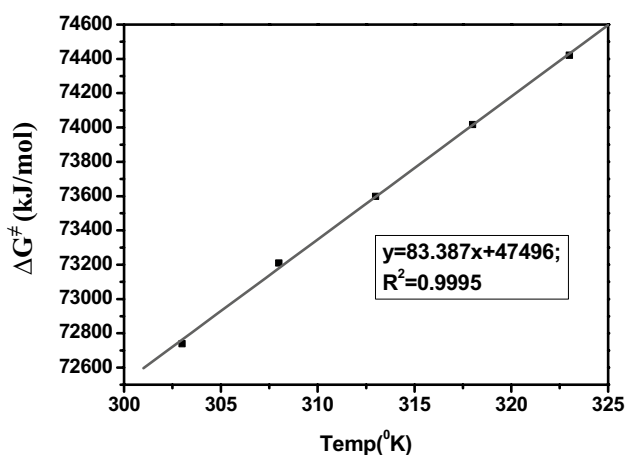


Fig. 18 Gibbs-Helmholtz plot (ΔG^\ddagger vs temperature) for PMS/ NaNO_2 mediated nitration of *P-Cresol*

nitration with a decreasing trend: $m\text{-Me} > P\text{-MeO} > \text{-H} > P\text{-Me} > m\text{-OH} > \approx P\text{-Br} \approx P\text{-OH} > P\text{-Cl}$. The ortho substituted phenols indicated a sequence: $o\text{-OH} > o\text{-Me} > \text{-H}$. Efforts were made correlate the rate data into Hammett's quantitative structure and reactivity relationship [31–33] using the following equation:

$$\log(k) = \log(k_0) \pm \sigma \rho$$

According to Hammett, $\log(k)$ versus (σ , the Hammett's substituent constant) a straight line with either a positive or negative slope (ρ ; Hammett's Rho) should be obtained.

But, the Hammett's plots of $\log(k)$ versus σ indicated poor linear relationship with very low correlation coefficient (R^2) and scattered points. The obtained deviations may be explained due to the mesomeric para interaction energy ($\Delta\Delta G_p$) parameters, and exalted sigma ($\bar{\sigma}$ or σ_{eff}) values, as suggested by Brown, Okamoto, van Bekkum, Webster and others [34, 35].

4 Conclusions

In summary, the author has developed peroxydisulfate (PDS) and peroxymonosulfate (PMS) as efficient green reagents for the nitration of aromatic compounds (Phenols) using $\text{NaNO}_2/\text{KHSO}_4$. The reaction followed second order kinetics with first order dependence on [Peroxy-Sulfate] (i.e. [PDS] or [PMS]) and [Phenol], when NaNO_2 concentration is taken far excess over all other reagents. The observed kinetic data is sensitive to the structural variation of phenol. Reaction rates accelerated with the introduction of electron donating groups and retarded with electron withdrawing groups: $m\text{-Me} > P\text{-MeO} > \text{-H} > P\text{-Me} > m\text{-OH} > \approx P\text{-Br} \approx P\text{-OH} > P\text{-Cl}$. On the other hand, ortho substituted phenols indicated a sequence: $o\text{-OH} > o\text{-Me} > \text{-H}$. But the data did not fit well into the Hammett's quantitative linear free energy relationship. Deviations could be probably due to mesomeric para interaction energy ($\Delta\Delta G_p$) parameters arising from the exalted sigma ($\bar{\sigma}$ or σ_{eff}) values, and Yukawa-Tsuno parameter (r).

Table 3 Second order rate constants and activation parameters for PS/NaNO₂ and PMS/NaNO₂ reactions (PS = PDS or PMS)

Substrate	PDS-NaNO ₂ system					PMS-NaNO ₂ system				
	Temp (K)	k (dm ³ /mol/s)	ΔG [‡] (kJ/mol)	ΔH [‡] (kJ/mol)	-ΔS [‡] (J/K/mol)	Temp (K)	k (dm ³ /mol/s)	ΔG [‡] (kJ/mol)	ΔH [‡] (kJ/mol)	-ΔS [‡] (J/K/mol)
Phenol	298	0.98	73.0	25.1	160.6	303	0.38	76.7	36.6	132.43
	308	1.44	74.6			308	0.50	77.3		
	318	2.12	76.0			318	0.80	78.6		
	323	2.26	77.1			323	1.00	79.3		
P-Cresol	298	1.92	71.3	51.7	66.2	303	1.82	72.7	47.4	83.40
	308	3.66	72.1			308	2.46	73.2		
	318	7.48	72.7			318	4.60	74.0		
	323	10.38	73.0			323	6.20	74.4		
Quinol	298	0.60	74.2	15.4	196.9	303	0.44	76.3	8.3	224.81
	313	1.00	76.8			308	0.46	77.5		
	318	1.02	78.0			313	0.48	80.0		
	323	1.04	79.2			323	0.60	80.7		
P-chloro phenol	298	0.34	75.7	50.8	83.5	303	0.16	78.9	72.8	19.81
	308	0.62	76.8			308	0.26	79.0		
	318	1.30	77.3			318	0.66	79.1		
	323	1.76	77.8			323	1.02	79.3		
P-Bromo phenol	298	0.48	74.8	19.7	183.5	303	0.32	77.1	44.8	107.12
	308	0.88	76.0			308	0.40	77.9		
	318	0.96	78.1			318	0.72	78.9		
	323	1.00	79.3			323	1.02	79.3		
P-Methoxy phenol	298	1.84	71.4	23.2	161.0	303	2.26	72.2	15.9	184.51
	308	3.18	72.5			308	3.42	72.3		
	318	3.92	74.4			318	3.66	74.6		
	323	4.16	75.4			323	3.88	75.7		
m-Cresol	298	4.00	69.5	27.3	142.0	303	3.88	70.8	32.7	126.23
	308	5.40	71.1			308	4.38	71.7		
	318	8.74	72.3			318	7.10	72.9		
	323	9.80	73.1			323	9.00	73.4		
Resorcinol	298	1.36	72.2	33.5	129.9	303	2.88	71.6	1.8	230.16
	308	2.16	73.5			308	3.36	72.4		
	318	3.74	74.6			318	3.04	75.1		
	323	3.98	75.6			323	3.46	76.0		
m-chloro phenol	298	0.40	75.2	18.0	191.8	303	0.26	77.7	35.4	138.56
	308	0.56	77.0			308	0.38	78.0		
	318	0.68	79.0			318	0.58	79.4		
	323	0.78	80.0			323	0.68	80.3		

Table 3 (continued)

Substrate	PDS-NaNO ₂ system				PMS-NaNO ₂ system				
	Temp (K)	k (dm ³ /mol/s)	ΔG [‡] (kJ/mol)	ΔH [‡] (kJ/mol)	Temp (K)	k (dm ³ /mol/s)	ΔG [‡] (kJ/mol)	ΔH [‡] (kJ/mol)	−ΔS [‡] (J/K/mol)
o-Cresol	298	4.80	69.0	17.6	303	4.26	70.6	26.9	144.10
	308	5.20	71.3		308	5.38	71.2		
	318	8.00	72.5		318	7.00	72.9		
	323	8.40	73.6		323	9.24	73.3		
Catechol	298	6.00	68.5	17.9	303	5.06	70.1	5.7	212.25
	308	6.22	70.8		308	6.04	70.9		
	313	6.48	71.9		313	6.00	72.1		
	318	5.42	73.6		318	6.12	73.2		
o-chloro phenol	298	0.40	75.2	25.9	303	0.36	76.8	27.1	163.64
	308	0.60	76.8		308	0.46	77.5		
	318	0.80	78.6		318	0.68	79.0		
	323	1.00	79.3		323	0.74	80.1		

10⁴[Phenol]=5.0 mol/dm³; 10⁴[PS]=5.0 mol/dm³; 10³[NaNO₂]=5.0 mol/dm³; 10³[KHSO₄]=5.0 mol/dm³; MeCN(% V/V) = 5.0

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Compliance with ethical standards

Conflict interest Authors declare that they don't have any competing financial interest.

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