

Sodium perborate/NaNO₂/KHSO₄-triggered synthesis and kinetics of nitration of aromatic compounds

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Abstract Sodium perborate (SPB) was used as efficient green catalyst for NaNO₂/ KHSO₄-mediated nitration of aromatic compounds in aqueous acetonitrile medium. Synthesis of nitroaromatic compounds was achieved under both conventional and solvent-free microwave conditions. Reaction times were comparatively shorter in the microwave-assisted than conventional reaction. The reaction kinetics for nitration of phenols in aqueous bisulfate and acetonitrile medium indicated firstorder dependence on [Phenol], [NaNO₂], and [SPB]. Reaction rates accelerated with introduction of electron-donating groups but retarded with electron-withdrawing groups. Kinetic results did not fit well quantitatively with Hammett's equation. Observed deviations from linearity were addressed in terms of exalted Hammett's constants ($\bar{\sigma}$ or σ_{eff}), *para* resonance interaction energy ($\Delta\Delta G_p$) parameter, and Yukawa–Tsuno parameter (r). This term provides a measure of the extent of resonance stabilization for a reactive structure that builds up charge (positive) in its transition state. The observed negative entropy of activation ($-\Delta S^{\#}$) suggests greater solvation and/or cyclic transition state before yielding products.

Keywords Kinetics · Mechanism · Sodium perborate/sodium nitrite/bisulfate · Nitration · Aromatic compounds · Hammett's equation · *para* resonance interaction energy $(\Delta\Delta G_p)$ parameter

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Introduction

Sodium perborate (SPB) is a crystalline, less toxic, inexpensive, and highly stable boron hydrate with formula NaBO₃ nH₂O (n = 1-6). It is a peroxo salt, being a highly useful reagent in organic synthesis and quite often used as a substitute for highly unstable hydrogen peroxide solutions. It is soluble in water and releases hydrogen peroxide, but is not merely a mixture of hydrogen peroxide and sodium borate. It is a stable, ecofriendly, and effective reagent in organic synthesis [1-20]. Kabalka noted that H₂O₂ sometimes requires guite harsh conditions that are incompatible with many functional groups, while SPB offers an interesting mild alternative [4–8]. In another publication, Kabalka's research group [9] revealed that SPB/boron trifluoride etherate is an effective reagent in dry tetrahydrofuran under chilled conditions (0 °C) for smooth hydroperoxide rearrangement of electron-rich and highly substituted benzylic tertiary alcohols to phenols. McKillop and coworkers observed that mixing SPB with acetic acid generates even more powerful oxidation species [10]. SPB oxidizes organic sulfides [11], anilines [12, 13], and indole [14] and enables uncatalyzed and Ru(III)-catalyzed oxidation of 5-oxoacids [15, 16] and oxidation of L-ascorbic acid [17]. SPB oxidizes organic compounds such as aromatic aldehydes, iodoarenes, and various sulfur heterocycles [18, 19]. Nitriles undergo smooth oxidative hydration to amides when aqueous methanol is employed as solvent. Firouzabadi et al. accomplished [20] conversion of several primary aromatic amines to corresponding nitrocompounds in good yield with SPB in micellar media using catalytic amount of tungstophosphoric acid (H₃PW·nH₂O). Pilarski and coworkers observed that SPB is a principal component of washing powders, and used it as an ecofriendly oxidant in palladium-catalyzed C-H acyloxylation of alkenes with excellent regio- and stereoselectivity [21]. This method enabled conversion of both terminal and internal alkenes, and even allowed benzylic C-H oxidation. Over the years, numerous useful methods have been developed for preparation of nitroaromatic compounds [22-26]. In a recent review, Guobing and Minghua [27] elaborately discussed several conventional and nonconventional synthetic protocols for nitration of aromatic compounds, including nitration of aromatic hydrocarbons, arylboronic acids, aryl halides and pseudohalides, and aryl carboxylic acids, and oxidation of aryl primary amines and azides. Our continued interest in development of ecofriendly synthetic protocols for nitration reactions, and their kinetic and mechanistic aspects [28-37], prompted us to pursue the present study into nitration of certain aromatic and heteroaromatic compounds under conventional and microwave-assisted conditions, using sodium perborate (SPB)/NaNO₂, in presence of KHSO₄. To gain insight into the mechanism of nitration, we also carried out kinetic study in aqueous acetonitrile medium.

Experimental

General

Reagent-grade sodium perborate (SPB), potassium bisulfate (KHSO₄), sodium nitrite (NaNO₂), and phenols were obtained from Avra, Aldrich, Merck, or SD Fine Chemicals. High-performance liquid chromatography (HPLC)-grade acetonitrile was used throughout for kinetic studies. Laboratory distilled water was further purified over permanganate and distilled twice, while other organic solvents were fractionally distilled before use. Isolated products of reactions were characterized by spectroscopic methods and physical data such as melting/boiling points. Infrared (IR) spectra were recorded on a PerkinElmer FT-IR spectrometer. ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Varian VNMRS-300 MHz spectrometer. Chemical shifts are reported in ppm relative to CHCl₃ (7.26) with tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a ZAB-HS mass spectrometer using electrospray ionization (ESI). Melting points were recorded using a Büchi B-545 capillary melting point apparatus.

General procedure for synthesis of nitrocompounds

For nitration, constituent reactants such as sodium nitrite (12 mmol) were mixed with aromatic or heteroaromatic compound (10 mmol), KHSO₄ (1 mmol), and catalytic amount of SPB (1 mmol). The mixture was refluxed at 60 °C for appropriate time then treated with NaHCO₃ solution and extracted with ethyl acetate (30 mL). The organic layer was separated, dried over Na₂SO₄, and evaporated under vacuum. Crude compound was purified by column chromatography using binary mixture of ethylacetate and hexane as eluent. This procedure afforded 2-nitrophenols as major product (80 %) and 4-nitrophenol in smaller proportion (20 %). These products were characterized by physical data and spectroscopic methods: ¹H NMR (300 MHz, CDCl₃): δ 9.56 (s, 1H, OH), 8.19 (dd, 1H, J = 9.1 Hz, J = 7 Hz), 7.59 (s, 1H, J = 8 Hz J = 7.5 Hz) 6.99 (d, 1H, J = 8.5 Hz) 9.18 (d, 1H, J = 8 Hz); m/z = 139; melting point = 45–49 °C). The same regioselective change was observed when aniline underwent nitration, affording *para* 4-nitroaniline as major component (80 %), whereas 2-nitroaniline was observed in only smaller proportion (20 %).

Microwave (MW)-assisted procedure for synthesis of nitrocompounds

Reactants such as sodium nitrite (12 mmol), with aromatic or heteroaromatic compound (10 mmol), KHSO_4 (1 mmol), and SPB (1 mmol), were thoroughly mixed with silica gel and placed in MW oven. Reaction progress was monitored by thin-layer chromatography (TLC) until completion. The reaction mixture was then treated with NaHCO₃ solution and extracted with ethyl acetate (30 mL). Final product was obtained by using the same workup steps as detailed in the preceding section. Sodium perborate/NaNO₂/KHSO₄-initiated nitration reactions with several

other compounds also afforded corresponding nitroderivatives (Scheme 1) via both conventional and MW-assisted reactions.

Method of following reaction kinetics

Stock solutions required for each set of experiments were always prepared fresh and stored in amber-colored bottles in a refrigerator. Requisite amounts of each reagent were pipetted out into reaction flasks, and the contents thermally equilibrated at desired temperature for about 20 min in a constant-temperature bath with accuracy of ± 0.1 °C. Reaction flask A contained requisite amounts of aqueous SPB and bisulfate, while flask B contained required amounts of phenol and nitrite. The reaction was initiated by rapid addition of thermally equilibrated flask A (perborate, bisulfate) to flask B solution. Progress of the reaction kinetics was followed spectrophotometrically at 405 nm, because most of the nitrophenols absorb at around 400 nm. Aliquots of reaction mixture were withdrawn into matched cuvette of 1 cm length and placed in the thermostatic cell compartment. Absorbance (or optical density, OD) of nitroaromatic compound (product) at given time t is defined as (A_i) while A_0 is the absorbance (if any) before reaction onset and the absorbance at infinite time (at the end of reaction) is A_{∞} , thus $(A_{\infty} - A_{t})$ is proportional to (a - x), the concentration of reactant at any given time, while $(A_{\infty} - A_0)$ is proportional to the initial concentration of the reactant (a).

Salient kinetic features of reaction

The reaction kinetics was followed under isothermal conditions, using requisite amounts of phenol, SPB, and NaNO₂ in aqueous acetonitrile media. In all experiments, [NaNO₂] was taken in large excess over [SPB], i.e., [NaNO₂]₀ >> [-SPB]₀, in aqueous acetonitrile medium, so that in situ-generated [NO₂⁺] was equal to [SPB]₀. Under pseudoconditions ([Phenol] = [NaNO₂]₀ >> [SPB]₀), and kinetic plots of ln[$(A_{\infty} - A_0)/(A_{\infty} - A_t)$] versus time passing through the origin indicated first order in [SPB] (Figs. 1, 2). The observed first-order rate constant, k', was evaluated from the slope of these plots. The plot of k' versus [Substrate] was linear, passing through the origin (under otherwise similar conditions), indicating first-order dependence on [Substrate]. Results for phenol, *p*-cresol, and *p*-bromophenol as typical examples are shown in Fig. 3. On the other hand, plots of $1/(A_{\infty} - A_t)$ versus time were found to be linear with positive gradient and definite intercept on



Scheme 1 Nitration of aromatic compounds under different conditions



Fig. 1 Pseudo-first-order plot for nitration of some phenols. 10^3 [Substrate] = 5.0 mol/dm³; 10^4 [SPB] = 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. Substrate = (a) *p*-cresol, (b) phenol, (c) *p*-catechol



Fig. 2 (*k*') versus [Sub] in SPB/NaNO₂-mediated nitration reaction of phenols. 10^4 [SPB] = 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 (*k*') versus [Sub] in SPB/NaNO₂-mediated nitration reaction of phenols. 10^4 [SPB] = 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

ordinate (vertical axis) under pseudo-second-order conditions ([NaNO₂]₀ >> [-SPB]₀ = [S]₀). These observations suggest that the reaction follows overall second-order kinetics (Fig. 4). Second-order rate constants were obtained from (k'/[S]), because k' = k[S] under pseudoconditions. The rate constants measured were found to be reproducible to ± 3 to ± 5 %. Correlation coefficients (R^2) of the linear regressions were usually higher than 0.990.

Effect of [Additives]

To provide insight into the mechanism and rate law, the rate dependences on [SPB], [NaNO₂], and [KHSO₄] were also investigated. Rate data (Table 1) revealed that variation in [KHSO₄] (0.005–0.050 mol/dm³), [NaNO₂] (0.001–0.010 mol/dm³), and [SPB] (0.001–0.002 mol/dm³) under otherwise similar conditions did not affect the rate to any significant extent. Together, these observations probably indicate that SPB is a stoichiometric reagent that generates nitronium ion in situ in presence of mild acid obtained from dissociation of bisulfate anion (HSO₄⁻). Furthermore, the constancy in the k' values with increase in [SPB] confirms the unity order with respect to [SPB].

Test for free radicals

To detect whether free radical intermediates were formed in situ during the course of the reaction, olefin monomers such as freshly prepared acrylamide or deareated acrylonitrile were added to the reaction mixture under nitrogen atmosphere. Sodium perborate (SPB) did not initiate/induce polymerization of added olefinic monomers even after 24 h under reflux conditions, indicating absence of free radical



Fig. 4 Second-order plots for some phenols. 10^4 [Substrate] = 5.0 mol/dm³; 10^4 [SPB] = 5.0 mol/dm³; 10^3 [NaNO₂] = 5.0 mol/dm³; 10^3 [KHSO₄] = 5.0 mol/dm³; MeCN (% V/V) = 5.0; temperature = 303 K: (a) *p*-chlorophenol, (b) phenol

10 ⁴ [SPB] (mol/ dm ³)	10 ³ [NaNO ₂] (mol/ dm ³)	[KHSO ₄] (mol/ dm ³)	$10^2 k' \text{ (min)}$
5.00	5.00	0.005	0.900
5.00	5.00	0.010	0.786
5.00	5.00	0.015	0.872
5.00	5.00	0.020	0.860
5.00	5.00	0.025	0.875
5.00	5.00	0.050	0.887
5.00	1.00	0.010	0.920
5.00	2.00	0.010	0.905
5.00	4.00	0.010	0.867
5.00	8.00	0.010	0.912
5.00	10.0	0.010	0.915
10.0	20.0	0.010	0.867
15.0	20.0	0.010	0.912
20.0	20.0	0.010	0.915

Table 1 Effect of variation of [Additives] on pseudo-first-order rate constant (k') in SPB/NaNO₂-mediated nitration reaction of phenol. 10^3 [Phenol] = 5.0 mol/dm³; MeCN (% V/V) = 5.0; temperature = 303 K

intermediates. To provide further insight into this aspect, we conducted kinetic experiments separately in presence of efficient radical scavengers such as mercuric chloride (HgCl₂) and allyl acetate. Addition of these additives over a wide concentration range (Table 2) did not alter the rate constant (k') of nitration to any significant extent. If radical intermediates were predominant, the rate of nitration would have decreased, because active free radicals should have been trapped by the scavengers. More particularly, HgCl₂ (mercuric chloride) should have been reduced

Table 2 Effect of variation of [Radical Scavengers] on pseudo-first-order rate constant (k') of SPB/NaNO2-mediated nitration reaction of phenol. 10^3 [Phenol] = 5.0 mol/dm³; 10^4 [SPB] = 5.00 (mol/dm³); 10^3 [NaNO2] = 8.00 (mol/dm³); [KHSO4] = 0.010 (mol/dm³); MeCN (% V/V) = 5.0;temperature = 303 K

Radical scavenger	10 ³ [Radical Scavenger] (mol/dm ³)	wenger] (mol/dm ³) $10^2 k'$ /min		
Normal reaction	Nil	0.912		
HgCl ₂	1.00	0.905		
	2.00	0.898		
	4.00	0.926		
	8.00	0.902		
Allyl acetate	1.00	0.925		
	2.00	0.912		
	4.00	0.910		
	8.00	0.904		

to HgCl (mercurous chloride), forming a precipitate. We did not observe any such precipitate. This observation may further lend support to our contention that nitration occurs through an ionic path but not by a free radical mechanism.

Results and discussion

Data in Table 3 show that phenols underwent nitration smoothly and gave corresponding nitration products in excellent yield, using both conventional and microwave-assisted (MWA) protocols. However, the reactions using the conventional protocol required longer reaction time. This difference can be explained by considering the fractions of reactive species which are activated under the conventional and MWA protocols. When using the MWA protocol, the fraction of activated species is far greater than obtained in the conventional reaction. This can be attributed to the instantaneously increased high temperature in MWA reactions, supplied directly to all reactant species without any heat loss. Such an increase in temperature is not possible in conventional thermal reactions, as explained in literature reports [36, 37].

Reactive species and mechanism of nitration

Literature reports on X-ray crystallographic studies reveal that the structure of sodium perborate (SPB) is Na₂X·6H₂0 [38, 39], exhibiting two Na⁺ ions, six water molecules, and the centrosymmetric cyclic anion, X^{2-} (where $X^{2-} = [B_2(O_2)_2(-OH)_4]^{2-}$). In the anion, boron atoms are joined by two peroxo bridges and their

Entry	Substrate	Product	Conventional		MWAS	
			R.t. (h)	Yield (%)	R.t. (s)	Yield (%)
1	Phenol	2-NO ₂ Phenol	7	68	90	70
2	o-Cresol	2-Me-4-NO ₂ Phenol	7	70	70	70
3	p-Cresol	2-NO ₂ 4-Me Phenol	7	75	70	75
4	m-Cresol	3-Me-4-NO ₂ Phenol	7	65	75	70
5	o-Cl Phenol	4-NO ₂ 2-Cl Phenol	8	75	90	75
6	m-Cl Phenol	4-NO ₂ 3-Cl Phenol	8	75	100	75
7	p-Cl Phenol	2-NO ₂ 4-Cl Phenol	8	70	90	78
8	p-Br Phenol	2-NO ₂ 4-Br Phenol	8	74	120	75
9	p-Nitrophenol	2,4-Dinitrophenol	10	70	180	78
10	Catechol	4-Nitrobenzene-1,2-diol	7	75	65	82
11	Resorcinol	2-Nitrobenzene-1,3-diol	7	75	75	75
12	Quinol	2-Nitrobenzene-1,4-diol	7	75	65	82
13	Salicylic acid	2-OH 4-NO ₂ Benzoic acid	7	75	120	75

 Table 3
 SPB/NaNO₂/KHSO₄-mediated nitration of organic compounds

tetrahedral coordination is completed by terminal OH groups [40–45]. In aqueous acid medium, SPB may exist as perborate anion, perboric acid, and H_2O_2 . Earlier, it was also mentioned that sodium perborate is not peroxoborate but borate peroxyhydrate; H_2O_2 acquires stronger electrophilicity by coordination with boric acid, which acts as a Lewis rather than protic acid. Extensive conductometric and cryoscopic investigations [44, 45] on borate— H_2O_2 systems revealed that H_2O_2 is associated with borate, thus supporting the above contention. It is also interesting to note [36, 37] that perborate exists as monomer, in solution of below 0.05 mol/dm⁻³ concentration in [B(OH)₄(H₂O₂)]⁻ and/or [B(OH)₃(H₂O₂)] forms of SPB, according to the following dissociation equilibrium:

$$\left[\mathbf{B}(\mathbf{OH})_{3}(\mathbf{H}_{2}\mathbf{O}_{2})\right] + \mathbf{H}_{2}\mathbf{O} \stackrel{K_{h}}{\rightleftharpoons} \left[\mathbf{B}(\mathbf{OH})_{4}(\mathbf{H}_{2}\mathbf{O}_{2})\right]^{-} + \mathbf{H}^{+}$$
(1)

The hydrolytic constant (K_h) of the above step was found to be in the range of 10^{-8} [40–43]. NMR and Raman spectroscopy indicate that, in dilute solution, an equilibrium exists that still contains peroxoborate anions [40–43]. This equilibrium is faster than the NMR time scale and is detected by a downfield shift in the time-averaged B-peak for the whole system [8]. In the present study, the reactions were conducted in presence of protic KHSO₄ salt, which dissociates easily to release H⁺ according to the following equilibrium:

$$\mathrm{HSO}_{4}^{-} \stackrel{K_{\mathrm{d}}}{\rightleftharpoons} \mathrm{H}^{+} + \mathrm{SO}_{4}^{-2} \tag{2}$$

$$\mathrm{H}^{+} + \mathrm{NO}_{2}^{-} \stackrel{\mathrm{A}_{1}}{\rightleftharpoons} \mathrm{HNO}_{2} \tag{3}$$

The dissociation constant (K_d) of (HSO_4^-) is about 10^{-2} , and the K_d/K_h ratio is about 10^6 , i.e., $K_d/K_h = 10^6$. Therefore, hydrolysis of $[\text{H}_3\text{BO}_3(\text{H}_2\text{O}_2)]$ can be suppressed in presence of KHSO₄. In otherwards equilibrium (1) shifts to the left, suggesting formation of $[\text{B}(\text{OH})_3(\text{H}_2\text{O}_2)]$ or $[\text{H}_3\text{BO}_3(\text{H}_2\text{O}_2)]$ during the course of the reaction. The reactive species $[\text{B}(\text{OH})_3(\text{H}_2\text{O}_2)]$ thus formed in turn might oxidize nitrite (NO_2^-) and generate in situ transient nitronium ion (NO_2^+) electrophile through the following sequence of steps:

$$\left[\mathbf{B}(\mathbf{OH})_{3}(\mathbf{H}_{2}\mathbf{O}_{2})\right] + \mathbf{HNO}_{2} \stackrel{K_{2}}{\rightleftharpoons} \mathbf{NO}_{2}^{+} + \left[\mathbf{B}(\mathbf{OH})_{4}\right]^{-} + \mathbf{H}_{2}\mathbf{O}$$
(4)

In presence of H^+ , transient HNO_3 might generate active nitronium (NO_2^+) species responsible for electrophilic nitration of aromatic compounds

$$NO_{2}^{+} + R - C_{6}H_{4} - X \xrightarrow{Slow(k_{1})} R - C_{6}H_{3} - X - (NO_{2}) + H^{+}$$

$$\tag{5}$$

For the above sequence of mechanistic steps (2-5), the rate law can be derived according to the following steps:

Rate =
$$-d[R-C_6H_4-X]/dt = k_1[NO_2^+][R-C_6H_4-X]$$
 (6)

From step (4)
$$[NO_2^+] = K_2 [B(OH)_3(H_2O_2)] [HNO_2] / [B(OH)_4]^-$$
 (7)

However, from step (3), in situ-produced $[HNO_2] = K_1[H^+][NO_2^-]$; substituting for $[HNO_2]$ in Eq. (7) gives

$$\left[\mathrm{NO}_{2}^{+}\right] = K_{1}K_{2}[\mathrm{SPB}]\left[\mathrm{NO}_{2}^{-}\right][\mathrm{H}^{+}]/[\mathrm{B}']$$

$$\left(\mathrm{Where}[\mathrm{SPB}] = \left[\mathrm{B}(\mathrm{OH})_{3}(\mathrm{H}_{2}\mathrm{O}_{2})\right]; [\mathrm{B}'] = \left[\mathrm{B}(\mathrm{OH})_{4}\right]^{-}\right)$$

$$\left(\mathrm{Where}[\mathrm{SPB}] = \left[\mathrm{B}(\mathrm{OH})_{3}(\mathrm{H}_{2}\mathrm{O}_{2})\right]; [\mathrm{B}'] = \left[\mathrm{B}(\mathrm{OH})_{4}\right]^{-}\right)$$

$$\left(\mathrm{Where}[\mathrm{SPB}] = \left[\mathrm{B}(\mathrm{OH})_{3}(\mathrm{H}_{2}\mathrm{O}_{2})\right]; [\mathrm{B}'] = \left[\mathrm{B}(\mathrm{OH})_{4}\right]^{-}\right)$$

Now, $[H^+]$ can be obtained from the dissociation step of (HSO_4^-) as

$$[\mathrm{H}^+] = \left(K_{\mathrm{d}} [\mathrm{HSO}_4^-] \right) / \left[\mathrm{SO}_4^{-2} \right]$$
(9)

Upon further substitution of $[H^+]$ from Eq. (9) into Eq. (8), followed by proper simplification, active species $[NO_2^+]$ can be obtained as

$$\left[\mathrm{NO}_{2}^{+}\right] = \frac{K_{\mathrm{d}}K_{1}K_{2}[\mathrm{SPB}]\left[\mathrm{NO}_{2}^{-}\right]_{t}\left[\mathrm{HSO}_{4}^{-}\right]}{[\mathrm{B}']\left[\mathrm{SO}_{4}^{-2}\right]}$$
(10)

Substituting the active species $[NO_2^+]$ from Eq. (10) into Eq. (6), the final rate law can be written as

Rate =
$$-d[R-C_6H_4-X]/dt = \frac{k_1K_dK_1K_2[SPB]_t[NO_2^-]_t[HSO_4^-][R-C_6H_4-X]_t}{[B'][SO_4^{-2}]}$$

(11)

The above rate equation is in accordance with the observed kinetic results, viz. first order in [Substrate] (i.e., $R-C_6H_4-X$) and [SPB]. Since $[NO_2^-]_t$ is taken in large excess over $[SPB]_t$ and $[KHSO_4]$, it implies that the order in [active NO_2^+ species] is also one. The bisulfate term ($[HSO_4^-]$) in the numerator of the rate law is canceled by the sulfate (SO_4^{-2}) term in the denominator, thus accounting for the observed marginal (HSO_4^-) effect on the reaction rate. At constant (HSO_4^-) concentration and known excess, the rate law reduces to

Rate =
$$-d[R-C_6H_4-X]/dt = k[NO_2^+][R-C_6H_4-X]$$

(Where $[NO_2^+] = (K_dK_1K_2[SPB]_t[NO_2^-]_t[HSO_4^-])/([B'][SO_4^{-2}])$

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

Temperature effect on rate of nitration

The SPB-catalyzed KHSO₄/NaNO₂-triggered nitration of various aromatic compounds was studied at different temperatures in the range of 300–325 K. The free energy of activation ($\Delta G^{\#}$) at various temperatures was calculated for the second-



Scheme 2 Mechanism of nitration of aromatic compounds

order rate constant (k) using Eyring's theory of reaction rates [40-43] using Eyring's equation according to the following steps:

$$\Delta G^{\#} = RT \ln \left(RT / Nhk \right)$$

Substituting $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $N = 6.022 \times 10^{23} \text{ mol}^{-1}$, $h = 6.626 \times 10^{-34} \text{ J s gives}$

$$(R/Nh) = \left[8.314/(6.022 \times 10^{23} \times 6.626 \times 10^{-34})\right] = 2.0836 \times 10^{10}$$
$$\ln(R/Nh) = \ln(2.0836 \times 10^{10}) = 0.7341 + 23.03 = 23.7641$$

 $\Delta G^{\#}$ could be simplified as: $\Delta G^{\#} = 8.314T[23.7641 + \ln(T/k)]$

Proper substitution of the temperature (*T*) in Kelvin and second-order rate constant (*k*), $\Delta G^{\#}$ is obtained in J/mol, which in turn can be easily converted to kJ/mol by dividing by 1000. The enthalpy and entropy of activation ($\Delta H^{\#}$ and $\Delta S^{\#}$) were obtained from the slope and intercept values of the Gibbs–Helmholtz plot of $\Delta G^{\#}$ versus temperature (*T*) (Fig. 5), according to the following relationship:

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#}.$$

Activation parameters for the nitration of various phenols are compiled in Table 4.

Quantitative structure and reactivity study

Closer inspection of the kinetic data pertaining to the SPB-catalyzed nitration of phenols reveals that introduction of electron-donating groups (EDG) into the aromatic ring accelerated the rate of nitration, while electron-withdrawing groups



Fig. 5 Gibbs–Helmholtz plot ($\Delta G^{\#}$ versus temperature) for nitration of some phenols. Substrate = (a) phenol, (b) *p*-cresol, (c) *o*-Cl phenol

(EWG) retarded the reaction rate with a decreasing trend: m-Me > p-MeO > - H > p-Me > m-OH > $\approx p$ -Br $\approx p$ -OH > p-Cl. On the other hand, *ortho*-substituted phenols indicated the following sequence: o-OH > o-Me > -H. The obtained data were cast into Hammett's quantitative structure and reactivity relationship [46, 47] with a view to analyze the kinetic data quantitatively, which in turn would be useful to understand the reaction mechanism.

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

According to Hammett, a plot of $\log(k)$ versus σ (Hammett's substituent constant) should show a straight line with either positive or negative slope (ρ ; Hammett's rho). A negative ρ value indicates that electron-donating substituent accelerates the reaction rate, with electron flow away from aromatic ring in the rate-determining step, thus producing electron deficiency (often a positive charge) in the activated complex. In the present study, Hammett's plots of $\log(k)$ versus σ indicated poor linear relationships with very low correlation coefficient (R^2) and negative slope value with ($\rho < 0$), indicating attack of an electrophile on the aromatic ring. Closer inspection of the data revealed that *para*-substituted derivatives scattered from linearity. The observed deviations can be explained by the mesomeric *para* interaction energy ($\Delta\Delta G_p$) parameter. For this purpose, the effective sigma ($\bar{\sigma}$ or σ_{eff}) values were calculated as suggested by Brown, Okamoto, van Bekkum, Webster, and others [48–55].

$$(\bar{\sigma} \text{ or } \sigma_{\text{eff}}) = (\log k - \log k_0)/\rho_{\text{m}},$$

where $\rho_{\rm m}$ is the modified reaction constant obtained for the Hammett's plot after removing the scattered points.

Substrate	Temp. (K)	k (dm ³ /mol/ s)	$\Delta G^{\#}$ (kJ/mol)	Equation and R^2	$\Delta H^{\#}$ (kJ/mol)	$-\Delta S^{\#}$ (J/ K/mol)
Phenol	303	1.80	72.8	v = 185.2x + 16.428	16.43	185.2
	308	2.41	73.3	$R^2 = 0.987$		
	313	2.60	74.3			
	318	2.82	75.3			
	323	3.02	76.4			
p-Cresol	303	1.23	73.8	y = 136.3x + 32,455	32.45	136.3
	308	1.62	74.3	$R^2 = 0.985$		
	313	1.81	75.2			
	318	2.20	76.0			
	323	3.01	76.4			
p-Bromophenol	303	0.400	76.6	y = 75.00x + 53,797	53.80	75.0
	308	0.601	76.8	$R^2 = 0.988$		
	313	0.800	77.4			
	318	1.20	77.6			
	323	1.60	78.1			
<i>p</i> -	303	2.41	72.0	y = 211.5x + 7792	7.79	211.5
Methoxyphenol	308	2.80	72.9	$R^2 = 0.990$		
	313	3.21	73.8			
	318	3.02	75.2			
	323	3.21	76.2			
m-Cresol	303	2.60	71.8	y = 84.59x + 46,178	46.18	84.59
	308	3.62	72.2	$R^2 = 0.996$		
	313	5.00	72.6			
	318	6.61	73.0			
	323	8.61	73.5			
Resorcinol	303	0.402	76.6	y = 115.5x + 41,358	41.36	115.5
	308	0.602	76.8	$R^2 = 0.970$		
	313	0.801	77.4			
	318	1.02	78.0			
	323	1.22	78.8			
m-Chlorophenol	303	0.140	79.2	y = 177.0x + 25,659	25.66	177.0
	308	0.151	80.4	$R^2 = 0.966$		
	313	0.200	80.0			
o-Cresol	303	1.02	74.2	y = 141.6x + 31,329	31.33	141.6
	308	1.21	75.0	$R^2 = 0.988$		
	313	1.61	75.6			
	323	2.21	77.2			
Catechol	303	3.02	71.5	y = 101.7x + 40,677	40.68	101.7
	308	3.81	72.1	$R^2 = 0.996$		
	313	5.22	72.5			
	323	8.61	73.5			

Table 4 Second-order rate constants and activation parameters for nitration of phenols

Substrate	Temp. (K)	<i>k</i> (dm ³ /mol/ s)	$\Delta G^{\#}$ (kJ/mol)	Equation and R^2	$\Delta H^{\#}$ (kJ/mol)	$-\Delta S^{\#}$ (J/ K/mol)
o-Chlorophenol	303 308 313 323	0.601 0.803 1.04 1.83	75.5 76.1 76.8 77.7	y = 109.7x + 42,296 $R^2 = 0.993$	42.30	109.7

Table 4 continued

$$-\Delta\Delta G_{\rm p} = 2.3RT\rho_{\rm m}(\bar{\sigma} - \sigma).$$

The $\Delta\Delta G_{\rm p}$ value indicates a less pronounced electron-withdrawing effect between the substituent and reaction center in the transition state than predicted. The Yukawa–Tsuno equation [46, 47] is one of the best modifications to the Hammett equation, quantifying the role of enhanced resonance effects on the reactivity of *meta-* and *para*-substituted aromatic compounds. This equation explains the enhanced resonance effects in electrophilic reactions of *para-* and *meta-*substituted organic compounds by introducing a new term (r) into the original Hammett relation. The Yukawa–Tsuno equation can take the following forms:

$$\log k = \log k_0 + \rho [\sigma + r(\sigma^+ - \sigma)],$$
$$\log k = \log k_0 + \rho [\sigma + r(\sigma^- - \sigma)],$$

where k_X and k_0 represent the rate constants for an X-substituted and unsubstituted compound, respectively, ρ represents the Hammett reaction constant, σ represents the Hammett substituent constant, σ^+ and σ^- represent the Hammett substituent constants for reactions in which positive or negative charge is built up at the reactive center, respectively, and *r* represents the Yukawa–Tsuno parameter. This term provides a measure of the extent of resonance stabilization for a reactive structure that builds up charge (positive) in its transition state. The negative entropy of activation ($-\Delta S^{\#}$) suggests greater solvation and/or cyclic transition state before yielding products (Table 5).

Conclusions

Sodium perborate (SPB) was investigated as efficient green catalyst for nitration of aromatic compounds (phenols) using NaNO₂/KHSO₄. The reaction followed second-order kinetics with first-order dependence on [SPB] and [Phenol]. Closer inspection of the kinetic data revealed that the reaction is sensitive to the structural variation of phenol. Reaction rates accelerated with introduction of electron-donating groups but retarded with electron-withdrawing groups in the following order: m-Me > p-MeO > -H > p-Me > m-OH > $\approx p$ -Br $\approx p$ -OH > p-Cl. On the other hand, *ortho*-substituted phenols indicated the following sequence: o-Me > o-

Temp.	Substituent	Effective sigma ($\bar{\sigma}$ or $\sigma_{\rm eff}$)	Hammett's sigma (σ)	$\Delta\Delta G_{\rm p}$ (kJ/mol)	Y–T parameter (<i>r</i>)
303 K	p-OMe	- 0.043	- 0.27	- 3.85	1.00
	<i>p</i> -Me	0.060	- 0.17	- 3.90	1.00
	<i>p</i> -Br	0.224	0.43	3.50	1.00
	p-Cl	0.327	0.23	- 1.64	1.00
	p-OH	0.224	- 0.37	- 1.00	1.00
308 K	p-OMe	- 0.021	- 0.27	- 4.67	1.00
	<i>p</i> -Me	0.056	- 0.17	- 4.23	1.00
	<i>p</i> -Br	0.190	0.43	4.49	1.00
313 K	p-OMe	- 0.029	- 0.27	- 4.51	1.00
	<i>p</i> -Br	0.164	0.43	- 4.98	1.00
318 K	<i>p</i> -Me	0.025	- 0.17	- 5.02	1.00
	<i>p</i> -Br	0.088	0.43	8.76	1.00
323 K	<i>p</i> -Me	0.0003	- 0.17	-4.57	1.00
	<i>p</i> -Br	0.064	0.43	9.83	1.00

Table 5 Exalted Hammett's constants and mesomeric *para* interaction energy ($\Delta\Delta G_p$) parameter

OH > -H. However, the results did not fit well with Hammett's quantitative linear free energy relationship. Deviations were suitably addressed by calculating exalted Hammett's constants ($\bar{\sigma}$ or σ_{eff}), mesomeric *para* interaction energy ($\Delta\Delta G_p$), and Yukawa–Tsuno parameters (*r*). The Yukawa–Tsuno parameter (*r*) provides a measure of the extent of resonance stabilization for a reactive structure that builds up charge (positive or negative) in its transition state.

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