Prussian Blue/NaNO₂ as an Efficient Reagent for the Nitration of Phenols in Aqueous Bisulfate and Acetonitrile Medium: Synthetic and Kinetic Study

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> ABSTRACT: The reaction kinetics of Prussian blue (PB)/NaNO2 initiated for the nitration of phenols by in aqueous bisulfate and acetonitrile medium indicated first-order dependence on [phenol], [NaNO₂], and [PB]. An increase in [KHSO₄] accelerated the rate of nitration under otherwise similar conditions. The rate of nitration was faster in the solvent of higher dielectric constant (D). Observed results were in accordance with Amis and Kirkwood plots [log k' vs. (1/D) and [(D - 1)/(2D + 1)]. These findings together with the linearity of plots, log k' versus (vol% of acetonitrile (ACN)) and mole fraction of (nx) ACN, probably indicate the importance of both eloctrostatic and nonelctrostatic forces, solvent-solute interactions during nitration of phenols. Reaction rates accelerated with the introduction of electron-donating groups and retarded with electron-withdrawing groups, which are interpreted by Hammett's theory of linear free energy relationship. Hammett's reaction constant (ρ) is a fairly large negative ($\rho <$ 0) value, indicating attack of an electrophile on the aromatic ring. Furthermore, an increase in temperature decreased the reaction constant (ρ) values. This trend was useful in obtaining isokinetic temperature (β) from Exner's plot of ρ versus 1/T. Observed β value (337.8 K) is above the experimental temperature range (303-323 K), indicating that the enthalpy factors are probably more important in controlling the reaction. \tilde{C} 2017 Wiley Periodicals, Inc. Int J Chem Kinet 49: 209-218, 2017

INTRODUCTION

Prussian blue (PB) pigment has got the distinction of being the first molecular coordination compounds (ferric ferrocyanide complex ($Fe_4[Fe(CN)_6]_3$), which was discovered by the German artist Diesbach in 1703 [1].

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For about three centuries, it is used as important ingredient in the preparation [1,2] of paints, printing inks, laundry dyes, etc. However, its structural, electronic, and magnetic properties and other transition metal analogues have been studied only in the past decade [2-7]. PB exists as water-soluble (KFe{Fe(CN)₆} \cdot xH₂O) and insoluble (Fe₄{Fe(CN)₆} \cdot 3yH₂O) forms [8]. PB and its analogues are used as efficient adsorbents in several catalytic processes [9], as well as an efficient tool for molecular separation [10] and for the removal of heavy metal ions in wine production [11], which could be attributed to their microporous character. PB exhibited several electrochemical applications for battery building [12], electronic switching, and as electrochromic devices [13]. PB has also been used as an efficient catalyst for H₂O₂ decomposition [14], transesterification of β -ketoesters [15], and epoxidation of styrene in the presence of tert-butyl hydroperoxide [16]. Recently, a team led by José Ramón Galán-Mascarós [17] revealed that Co-Fe Prussian blue coordination polymers could be effectively used for the oxidation of water. Recently, Adhikamsetty and Jonnalagadda reported the kinetics and mechanism of water-soluble PB formation [18].

Nitration of aromatic compounds is one of the most important electrophilic aromatic substitution reactions to introduce a nitrogroup into an aromatic ring of organic compound. It is used for the production of large varieties of nitroaromatics, which accomplished a broad spectrum of proven applications in the synthesis of new/small-sized materials, dyes, pharmaceuticals, perfumes, and plastics since the beginning of the 20th century. Several nitroaromatics are also used as solvents and chemical intermediates and precursors in the manufacture of synthetic dyestuffs and other chemicals. For a longer time, a mixture of concentrated sulfuric and nitric acids is used as a source for the generation of nitronium ion species, which is the active ingredient for nitration. However, a large amount of acid mixture is discharged through laboratory and industrial outlets, which is the root cause to trigger environmental issues. Several groups of researchers all over the world suggested different alternative protocols to to overcome these issues [19–21].

On the other hand, several kinetic and instrumentation studies have been taken up to understand the mechanism of nitration since the 1904 [22–33], which provided ample of evidence for the formation of nitronium ion (NO₂⁺). The kinetic studies taken up by Ingold's research group [27] and Martinsen [28] contributed enormously to understand the role of nitronium (NO₂⁺) and nitracidium (H₂NO₃⁺) ion species in the mechanism of nitration under different conditions. Gillespie's research group [24] suggested a noteworthy observation on the formation of the nitronium ion from freezing point studies. The dissolution of HNO_3 in 100% H₂SO₄ at the freezing point produces four ions, according to the following equilibrium:

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2 HSO_4^-$$

The existence of nitronium ion (NO_2^+) species has been further confirmed by x-ray crystallography and Raman spectroscopic studies [24-26]. Research reports of Kecki [29] and Miller et al. [30] furnished excellent literature and a detailed account of the role of acidity in the nitration of aromatic compounds from detailed kinetic studies. In another review, Kulkarni [31] highlighted four different approaches for continuous flow of nitration with microreactors. Enthused by the foregoing aspects on nitration reaction, we have also taken up a detailed colorimetric kinetic study comprising PB/NaNO2-initiated nitration of phenols in aqueous bisulfate and acetonitrile medium. Nevertheless, we have recently reported PB as an ecofriendly catalyst for selective nitration of organic compounds in the presence of small amounts of HNO₃ for the synthesis of nitroaromatics under conventional and nonconventional conditions [34], which is different from the present kinetic investigation.

EXPERIMENTAL

General

Chemicals used in this study are of reagent grade, which were purchased from Aldrich, Merck, Loba, or Fluka (India). Laboratory-made distilled water was further purified over permanganate and distilled twice, whereas other organic solvents were fractionally distilled before use. Products of the reactions were characterized by spectroscopic methods and physical data such as melting/boiling points, infrared (IR),¹H NMR, and mass spectroscopic studies.

Kinetic Method of Following the Reaction

A reaction flask containing known amounts of aqueous PB and NaNO₂ solutions and another flask containing phenol (prepared in acetonitrile) along with requisite amounts of KHSO₄ were thermostated in a constant temperature bath at a desired temperature. The reaction was initiated by mixing both sets of solutions thoroughly. In all the experiments, [NaNO₂] was taken large excess over [PB] ([NaNO₂]₀ \gg [PB]₀) in aqueous acetonitrile/KHSO₄ medium, so that in situ generated [NO₂⁺] was equal to [PB]₀. Black-coated flasks from outside were used to prevent photochemical effects. Aliquots of the reaction mixture were withdrawn into a cuvette and placed in electronically thermostated cell compartment of the spectrophotometer. The PB content could be estimated from the previously constructed calibration curve showing absorbance (A) versus [PB] at 430 nm. Absorbance values were in agreement with each other with an accuracy of $\pm 3\%$ error. For the purpose of kinetic studies, absorbance of nitrate species produced during the course of reaction at a given time is defined as (A_t) , whereas the absorbance at infinite time (at the end of the reaction) is considered as A_{∞} , and A_0 , the absorbance (if any) before the start of reaction. Thus $(A_{\infty} - A_t)$ is proportional to (a - x), the concentration of reactant at any given time, whereas $(A_{\infty} - A_0)$ is proportional to initial concentration of the reactant (a).

General Procedure for Synthesis of Nitrocompounds under Acid-Free Kinetic Conditions

For the purpose of product analysis, a separate reaction has been done under kinetic conditions, and progress of the reaction was monitored by TLC. After completion, the reaction mixture was treated with 5% sodium thiosulfate (hypo) solution. The organic layer was separated and dried over Na₂SO₄ and evaporated under vacuum. Column chromatography was used to purify crude product. A binary mixture of ethyl acetate and hexane (3:7) was used as an eluent to get a pure product 4-nitrophenol as a yellow powder (mp 111–113°C) in 85% yield, IR (KBr) (ν_{max}/cm^{-1}): 3331, 1614, 1592, 1500, 1346; ¹H NMR (300 MHz, CDCl₃): δ 9.95 (s 1H, OH), 6.95 (d 2H, J = 8Hz), 8.15 (d 2H, J =8Hz); m/z = 139.

PB/NaNO₂/KHSO₄-initiated reactions with several other phenols also afforded the corresponding nitrophenol derivatives (Scheme 1) in about 1–3 h under conventional stirred conditions at room temperature. All the products were characterized by physical data, ¹H NMR, and mass spectra, with authentic samples are found to be satisfactory and in consonance with our earlier reports [34].



Figure 1 Plot of $\ln [(A_{\infty} - A_0)/(A_{\infty} - A_t)]$ versus time (firstorder plot) at 318 K in 25% MeCN [phenol] = 0.05 mol/dm³; [NaNO₂] = 0.05 mol/dm³; [PB] = 0.001 mol/dm³; [KHSO₄] = 0.01 mol/dm³. [Color figure can be viewed at wileyonlinelibrary.com]

RESULTS AND DISCUSSION

Kinetic Observations in the Present Study

(i) The plots of $\ln [(A_{\infty} - A_0)/(A_{\infty} - A_t)]$ versus time were linear with positive slope passing through origin, under the conditions: $[NaNO_2]_0$, $[phenol]_0 \gg [PB)]_0$ (Fig. 1). This observation reveals first-order kinetics in [PB]. First-order rate constant (k') could be obtained from the slopes of these linear plots. Typical first-order rate constant data are presented in Table I. (ii) However, under pseudo–second-order conditions ($[NaNO_2]_0 \gg$ $[PB)]_0 = [S]_0$), plots of [1/(a - x)] or $(1/(A_{\infty} - A_t))$ versus time have been found to be linear with a positive gradient and a definite intercept on the ordinate (vertical axis) indicating overall second-order kinetics (Fig. 2).

From the forgoing kinetic observations, it is clear that order in [S] is also one, because order with respect to [PB] is verified as one under pseudoconditions (Figs. 1 and 2), and overall order is second order. Second-order rate constant values for nitration of phenols are compiled in Table II.

Computation of Activation Parameters

Rate constants increased substantially within an increase in the temperature. According to Eyring's theory



Scheme 1 Nitration of phenols under different conditions.

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Substrate	Temperature (K)	Equation and R^2	<i>k</i> ′ (min)
Phenol	300	$y = 0.010x - 0.028; R^2 = 0.991$	0.010
	313	$y = 0.015x + 0.037; R^2 = 0.990$	0.015
	323	$y = 0.028x - 0.088; R^2 = 0.989$	0.028
<i>p</i> -Cresol	300	$y = 0.015x - 0.036; R^2 = 0.989$	0.015
	313	$y = 0.018x - 0.054; R^2 = 0.987$	0.018
	323	$y = 0.032x - 0.094; R^2 = 0.977$	0.032
<i>p</i> -Cl phenol	300	$y = 0.007x - 0.006; R^2 = 0.990$	0.007
	313	$y = 0.011x - 0.011; R^2 = 0.990$	0.011
	323	$y = 0.024x - 0.024; R^2 = 0.993$	0.024
<i>m</i> -Cresol	300	$y = 0.014x + 0.031; R^2 = 0.992$	0.014
	313	$y = 0.016x + 0.0217; R^2 = 0.916$	0.016
	323	$y = 0.029x + 0.046; R^2 = 0.976$	0.029
Beta napthol	300	$y = 0.007x; R^2 = 0.996$	0.007
	313	$y = 0.019x - 0.030; R^2 = 0.976$	0.019
	323	$y = 0.026x + 0.0230; R^2 = 0.973$	0.026
<i>p</i> -nitrophenol	313	$y = 0.012x + 0.027; R^2 = 0.927$	0.012
	318	$y = 0.015x + 0.123; R^2 = 0.966$	0.015
	323	$y = 0.019x + 0.025; R^2 = 0.968$	0.019
Resorcinol	300	$y = 0.008x - 0.018; R^2 = 0.995$	0.008
	313	$y = 0.013x - 0.034; R^2 = 0.994$	0.013
	323	$y = 0.025x - 0.141; R^2 = 0.953$	0.025
Catechol	300	$y = 0.005x + 0.024; R^2 = 0.986$	0.005
	313	$y = 0.007x + 0.023; R^2 = 0.991$	0.007
	323	$y = 0.101x - 0.0182; R^2 = 0.993$	0.101
m-Chlorophenol	300	$y = 0.005x + 0.024; R^2 = 0.986$	0.005
	313	$y = 0.009x + 0.024; R^2 = 0.993$	0.009
	323	$y = 0.021x - 0.008; R^2 = 0.998$	0.021

Table IPseudo-First-Order Rate Constants (k') for Nitration of Phenols in 25% MeCN Medium

 $[Substrate] = 0.0125 \text{ mol/dm}^3; [NaNO_2] = 0.125 \text{ mol/dm}^3; [KHSO_4] = 0.0025 \text{ mol/dm}^3$

of reaction rates [35], free energy of activation ($\Delta G^{\#}$) can be correlated to the rate constant (*k*) at any given temperature,

$$k = (k_t) \left(RT/Nh \right) \exp\left(-\Delta G^{\#}/RT \right)$$
(1)



Figure 2 Plot of $[1/(A_{\infty} - A_t)]$ versus time (second-order plot) in 25% MeCN [phenol] = 0.001 mol/dm³; [NaNO₂] = 0.1 mol/dm³; [PB] = 0.001 mol/dm³; [KHSO₄] = 0.1 mol/dm³. [Color figure can be viewed at wileyonlinelibrary.com]

where the transmission coefficient (k_t) is equal to unity; R, N, h, and T represent the gas constant, Avogadro number, Planck's constant, and reaction temperature, respectively; and $\Delta G^{\#}$ represents free energy of activation. Rearrangement of the above equation gives

$$(Nhk/RT) = \exp\left(-\Delta G^{\#}/RT\right)$$
(2)

Natural logarithms for the above equation gives

$$\ln\left(Nhk/RT\right) = -\left(\Delta G^{\#}/RT\right) \tag{3}$$

Rearranging for $(\Delta G^{\#})$: $(\Delta G^{\#} = -RT \ln (Nhk/RT))$ (4)

Equation (4) is used to calculate the free energy of activation ($\Delta G^{\#}$) at various temperatures, and the Gibbs–Helmholtz equation (5) for the evaluation of enthalpy and entropies of activation ($\Delta H^{\#}$ and $\Delta S^{\#}$) and the representative plot (Fig. 3):

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	Temperature		ΔG^{\neq}		ΔH^{\neq} (kJ/mol)	$-\Delta S^{\neq}$ (J/K/mol)
Substrate	(K)	k	(kJ/mol)	Equation and R^2		
Phenol	300	0.8	74.05536	$y = 0.135x + 33.55; R^2 = 0.962$	33.55	135
	313	1.2	76.36342			
	318	1.76	76.56817			
	323	2.24	77.16634			
p-Cresol	300	1.2	73.04405	$y = 0.163x + 24.31; R^2 = 0.959$	24.31	163
	313	1.44	75.84523			
	318	2.16	76.02672			
	323	2.56	76.80776			
p-Cl Phenol	300	0.56	74.94498	$y = 0.114x + 40.69; R^2 = 0.920$	40.69	114
	313	0.88	77.12679			
	318	1.44	77.09871			
	323	1.92	77.5803			
<i>m</i> -Cresol	300	1.12	73.21613	$y = 0.168x + 23.03; R^2 = 0.954$	23.03	168
	313	1.28	76.15173			
	318	1.92	76.33812			
	323	2.32	77.07211			
Beta napthol	300	0.56	74.94498	$y = 0.100x + 44.67; R^2 = 0.917$	44.67	100
	313	1.52	75.70453			
	318	1.84	76.45064			
	323	2.08	77.36535			
<i>p</i> -nitrophenol	313	0.96	76.90036	$y = 0.056x - 16.58; R^2 = 0.993$	16.58	56
	318	1.2	77.58074	-		
	323	1.52	78.20766			
Resorcinol	300	0.64	74.61192	$y = 0.123x + 37.82; R^2 = 0.963$	37.82	123
	313	1.04	76.69207			
	323	2	77.47068			
Catechol	300	0.72	74.31815	$y = 0.160x + 26.16; R^2 = 0.988$	26.16	160
	313	1.04	76.69207	-		
	318	1.28	77.41011			
	323	1.68	77.93889			
m-Chlorophenol	300	0.4	75.7842	$y = 0.094x + 47.68; R^2 = 0.900$	47.68	94
	313	0.72	77.64899			
	318	1.2	77.58074			
	323	1.68	77.93889			

Table II Second-Order Rate Constants and Activation Parameters for Nitration of Phenols



Figure 3 Gibbs–Helmholtz plot of $\Delta G^{\#}$ versus *T* for nitration of *p*-nitrophenol. [Color figure can be viewed at wiley-onlinelibrary.com]

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#} \tag{5}$$

Effect of variation of [KHSO₄]. In the absence of KHSO₄, the reaction did not proceed even under reflux temperatures. Reactions triggered only in the presence of KHSO₄, and rate of the reaction enhanced with an increase in KHSO₄ concentration. The plots of k' versus [KHSO₄] were found linear passing through origin (Fig. 4), establishing the role of HSO₄⁻ in the generation of the active nitronium ion.

Reactive Species and Mechanism

Nature of the solvent and its properties are known to play an important role to influencing the reaction



Figure 4 Plot of *k'* versus [KHSO4]. [Color figure can be viewed at wileyonlinelibrary.com]

rates with or without influencing the reaction mechanism [36-42]. Kinetics of the nitration has been studied in different dielectric media using binary solvent mixtures of acetonitrile and water of different compositions, and the rate data are presented in Table III. This affords a change in the dielectric constant (D) of the medium. The authors tried to interpret the observed kinetic results using semiquantitative relationships developed by Amis, Laidler-Eyring, Kirkwood, Hughes, Ingold, and others [39,40], which are mainly concerned with the rate of the reaction (or rate constant) as a function of bulk dielectric constant (D). Accordingly, the plots of log k' versus 1/D has been found linear with negative slope (Fig. 5), whereas the plot of log k' versus [(D-1)/(2D+1)] was linear with positive slope (Fig. 6). These observations probably indicate the participation of anionic species and molecular or (dipolar) species in the rate-determining step. These observations may probably indicate the participation of anionic and molecular species in the rate-limiting step.

On the other hand, the plots of $\log k''$ versus volume percentage (vol%) and mole fraction (n_x) of acetonitrile



Figure 5 Plot of log *k* versus 1/*D*. [Color figure can be viewed at wileyonlinelibrary.com]

were also linear with negative slopes (Figs. 7 and 8). These observations probably indicate that apart from the dielectric constant, solvent–solute interactions, and other solvent properties might be important in controlling the reaction rates. This aspect could be supported from the suggestions of Robinson and Stokes [37] and findings of Brown and Hudson [38]. According to Robinson and Stokes [37], *the bulk dielectric constant is entirely different from internal dielectric constant especially in the solvent of low dielectric media*. Brown and Hudson have found that the rate of hydrolysis of acid chlorides in DMF is almost equal to 95% dioxane in spite of the difference in their dielectric constants [38]. A perusal of literature depicts several such anomalies [41].

UV–Visible Spectroscopic Studies. Since the reactions are conducted in aqueous acetonitrile medium, sodium nitrite (NaNO₂) and KHSO₄ being strong electrolytes undergo dissociation to afford nitrite (NO₂⁻)

Table III Effect of Temperature/Solvent on Hammett's Reaction Constant (ρ)

Hammett's equation: $\log k = \log k_0 \pm \rho \sigma$									
Substrate	Hammett's σ	Rate Constant (k) at Given Temperature (T) (K)							
		300	313	318	323				
Phenol	0	0.8	1.2	1.76	2.24				
p-Cresol	-0.17	1.2	1.44	2.16	2.56				
p-Chloro	0.23	0.56	0.88	1.44	1.92				
<i>m</i> -Cresol	-0.07	1.12	1.28	1.92	2.32				
Resorcinol	0.12	0.64	1.04	1.60	2.00				
<i>m</i> -Chlorophenol	0.37	0.4	0.72	1.20	1.68				
Hammett's ρ (slope of Hammett's plot)		-0.903	-0.556	-0.455	-0.325				
Equation for the Exner's plot: ρ versus $1/T$		$\rho = A [1 - \beta/T] = A - (A\beta)/T$ $y = 2417x - 7.155; R^2 = 0.998$							
Isokinetic temperature	(β) value	337.8 К							



Figure 6 Plot of log k versus (D - 1)/(2D + 1). [Color figure can be viewed at wileyonlinelibrary.com]

Figure 7 Plot of $\log k$ versus MeCN%(v/v). [Color figure can be viewed at wileyonlinelibrary.com]

Figure 8 Plot of log *k* versus mole fraction (n_x) . [Color figure can be viewed at wileyonlinelibrary.com]

and bisulfate (HSO₄⁻). To have an insight into the interaction between PB with anionic species such as nitrite (NO₂⁻), bisulfate (HSO₄⁻), and molecular species such as acetonitrile, we have taken up an elaborate UV–visible spectroscopic study of PB under different conditions and results are presented in Figs. 9–12, respectively.

UV–visible spectrum of aqueous PB (Fig. 9) indicated two bands, one hump at 430 and the other broad band at 675–680 nm. This observation is in close agreement with that described by Jonnalagadda and Adhikamsetty [18]. When the spectrum of PB solution is scanned in aqueous acetonitrile, both the above-cited peaks underwent hypochromic shift (Fig. 10), indicating solvent (water)–solvent (ACN) and solvent (ACN)– solute (PB) interactions. These interactions might bring about some changes in the coordination spheres of Fe present in PB. When the spectrum of PB is scanned in aqueous acetonitrile medium containing KHSO₄, peak observed at 430 underwent a blueshift by 15 nm, while another broad band underwent a redshift from at

Figure 11 PB-KHSO $_4^-$ in aqueous ACN.

675-680 nm to 680-700 nm (Fig. 11). This observation could be attributed to a change in the coordination spheres of PB due to PB with the interaction of bisulfate ions. Finally, when the spectrum of PB is scanned in aqueous acetonitrile medium containing KHSO4 and NaNO₂ peak observed at 430 underwent a blueshift by 10 nm, whereas another broad band underwent a redshift from 675-680 to 675-700 nm followed by slight hyperchromic shift (Fig. 12). These changes could most probably suggest the interaction of PB with nitrite as well as with bisulfate. Furthermore, it is of interest to note that protonation of ferrocyanide ion as such is too fast and the $H[Fe((CN)_6]^{3-}$ ion is known to react with other species [18], but with its first protonation constant pK = 4.19, i.e., $K = 6.45 \times 10^{-5}$ [18]. Thus an increase in acid concentration could also lead to higher concentration of protonated PB [HFe{Fe($(CN)_6$ }] due to the reaction between H⁺ and Fe{Fe((CN)₆}⁻ ion (anionic form of soluble PB). In the present study, the rate of

Figure 12 PB-KHSO₄ $^-$ NaNO₂ in aqueous ACN.

nitration was enhanced with an increase in [KHSO₄]. Observed rate acceleration could be attributed to the available proton due to the dissociation of bisulfate into proton and sulfate ions according to the following equilibrium:

$$\mathrm{HSO}_{4}^{-} \rightleftharpoons \mathrm{H}^{+} + \mathrm{SO}_{4}^{2-} \tag{6}$$

Soluble-PB anion $(Fe{Fe((CN)_6}^-)$ then transforms into protonated-PB species $([HFe{Fe((CN)_6}]),$ as shown in the following equilibrium:

$$\operatorname{Fe} \{\operatorname{Fe}((\operatorname{CN})_6\}^- + \operatorname{H}^+ \rightleftharpoons \left[\operatorname{HFe} \{\operatorname{Fe}((\operatorname{CN})_6\}\right] \quad (7)$$
(Soluble PB anion)
(Protonated PB)

On the other hand, an interaction between and Fe(III)-enriched PB (hard acid) and SO_4^{2-} (hard base) is also more likely according to Pearson's Hard and soft acids and bases (HSAB) theory, because hard acid prefers to combine with hard base [42]. These foregoing kinetic features coupled with UV–visible spectroscopic results substantiate a plausible stepwise mechanism with the participation of [KHFeSO₄ (NO₂) [Fe ((CN)₆)²⁻]] and molecular species (RC₆H₄X) in the slow step as shown in Scheme 2.

Quantitative Structure Reactivity Study

An insight into the kinetic data of nitration of phenols revealed that the rates accelerated with the introduction of electron-donating groups and retarded with electron-withdrawing groups and found to follow the following sequence: p-Me > m-Me > H > o-OH > m-OH > m-OH > m-Cl.

Accordingly, Hammett's linear free energy relationships plots were tried to interpret these results. Hammett's log (k/k_0) versus σ plot (Fig. 13) exhibited very good linear relationship as evidenced from the correlation coefficient values (R^2), which were greater

Figure 13 Typical Hammett's plot at 318 K. [Color figure can be viewed at wileyonlinelibrary.com]

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Scheme 2 Plausible mechanism for nitration of phenols.

than 0.960 [43]:

$$\log\left(k/k_0\right) = \sigma\rho \tag{8}$$

The negative value of ρ indicates that the electron flow away from the aromatic ring takes place in the rate-determining step by producing electron-deficient transition state (often a positive charged activated complex). The rate-determining step for most electrophilic substitutions shows the electrophile reacts with the aromatic ring to form the arenium ion. Data presented in Table III revealed that the rho (ρ) values obtained from the present experiments are fairly large negative values ($\rho < 0$), indicating attack of an electrophile on the aromatic ring.

According to Exner [44,45], ρ values for a given reaction are influenced by the temperature according to the following relation:

$$(\rho) = A \left[1 - \beta / T \right] = A - A\beta / T$$

where A is a constant and β is the isokinetic temperature. When $\beta = T$, $\rho = 0$, thus isokinetic temperature is the temperature at which the effect of substituent on the rate of reaction vanishes and all the substituted compounds in a given series have the same reactivity. In the present study, the plot of rho (ρ) versus (1/*T*) gave a linear plot with slope of (*A* β), and intercept was equal to *A*. The obtained (slope/intercept) ratio afforded the isokinetic temperature (β) with a value of 338 K, which is above the experimental temperature range (303–323 K), suggesting that enthalpy factors are important in controlling the reaction. Large negative entropy values probably indicate the importance of greater solvation in the transition state. Put together, it appears that both entropy and enthalpy values are important in this study.

CONCLUSIONS

In summary, we have developed an acid-free protocol for nitration of phenols with PB/NaNO₂ in an aqueous bisulfate and acetonitrile medium. The reaction followed second-order kinetics with first-order dependence on [PB] and [phenol] when [NaNO₂] is taken large excess over [PB]. Rates of nitration (log k) were found to fit into either Amis or Kirkwood plots $[\log k'' \text{ vs. } (1/D) \text{ or } [(D-1)/(2D+1)].$ In addition to this, the observed results may also indicate the importance of equilibrium as well as frictional solvent effects and solvent-solute interactions for solvation of transition state during nitration of phenols. Reaction rates accelerated with the introduction of electron-donating groups and retarded with electron-withdrawing groups with the following sequence: p-Me > m-Me > H > o-OH > m-OH > m-Cl. The results are interpreted by Hammett's theory of linear free energy relationship. The reaction constant (Hammett's ρ) values obtained from the present experiments are fairly large negative values ($\rho < 0$), indicating attack of an electrophile on the aromatic ring. An increase in temperature decreases the reaction constant (ρ) values, and Exner's plot of ρ versus 1/T gave isokinetic temperature (β) with a value of 337 K, which is slightly higher than the experimental temperature range (303–323 K). This observation could probably suggest that enthalpy factors are important in controlling the reaction. Large

negative entropy values probably indicate the importance of greater solvation in the transition state.

BIBLIOGRAPHY

- 1. Woodward, J. Philos Trans 1724, 33, 15-17.
- (a) Dunbar, K. R.; Heintz, R. A. Prog Inorg Chem 1997, 45, 283; (b) Shatruk, M.; Dragulescu-Andrasi, A.; Chambers, K. E.; Stoian, S. A.; Bominaar, E. L.; Catalina Achim, C.; Kim, R.; Dunbar, K. E. J Am Chem Soc 2007, 129, 6104–6116.
- 3. Robin, M. B. Inorg Chem 1962, 1, 337-342.
- Sano, H.; Hashimoto, F. Bull Chem Soc Jpn 1965, 38, 684–685.
- 5. Walker, R. G.; Watkins, K. O. Inorg Chem 1968, 7, 885–888.
- Ito, A.; Suenaga, M.; Ono, K. J Chem Phys 1968, 48, 3597–3599.
- Mayoh, B.; Day, P. J Chem Soc, Dalton Trans 1976, 1483–1486.
- Balmaseda, J.; Reguera, E.; Fernandez, J.; Gordillo, A.; Yee-Madeira, H. J. Phys Chem Solids 2003, 64, 685.
- 9. Reguera, E.; Fernandez, J.; Duque J. Polyhedron 1994, 13, 479.
- Balmaseda, J.; Reguera, E.; Gomez, A.; Diaz, B.; Autie, M. Microporous Mesoporous Mater 2002, 54, 285.
- 11. Wenker, D.; Spiess, B.; Laugel, P.; Lapp, C. Food Addit Contam 1989, 6, 351.
- 12. Neff, V. D. J Electrochem Soc 1985, 132, 1382.
- (a) DeBerry, D. W.; Viehbeck, A. J Electrochem Soc 1983, 130, 249; (b) Gadet, V.; Mallah, T.; Castro, I.; Verdaguer, M. J Am Chem Soc 1992, 114, 9213.
- 14. Uyanik, G.; Pekin, B. J Catal 1970, 19, 195-203.
- Srinivas, P.; Rajanna, K. C.; Krishnaiah, G.; Satish Kumar, M.; Narender Reddy, J. Synth React Inorg Met-Org Nano-Met Chem 2014, 44, 1212–1220.
- Liang, Y.; Yi, C.; Tricard, S.; Fang, J.; Zhao, J.; Shen, W. RSC Adv 2015, 5, 17993–17999.
- Pintado, S.; Goberna-Ferrón, S.; Escudero-Adán, E. C.; Galán-Mascarós, J. R. J Am Chem Soc 2013, 135, 13270–13273.
- Adhikamsetty, R. K.; Jonnalagadda, S. B. Bull Chem Soc Ethiop 2009, 23, 47–54.
- (a) Booth, G. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, Germany 2005;
 (b) Olah, G. A.; Malhotra, R.; Narang, S. C. Nitration Methods and Mechanisms (Organic Nitro Chemistry Series), Vol. A17; VCH: New York, 1989, p. 411–455 (1991).
- (a) Hoggett, J. G.; Monodie, R. B.; Penton, J. R.; Schofield, K. Nitration and Aromatic Reactivity; Cambridge University Press: London (UK), 1971; (b) Ono, N. The Nitro Group in Organic Synthesis; Wiley-VCH: New York, 2001.
- (a) Olah, G. A.; Kuhn, S. J. Org Synth Coll 1973, 5, 480;
 (b) Olah, G. A.; Kuhn, S. J. Org Synth Coll 1967, 47, 56;
 (c) Surya Prakash, G. K.; Mathew, T. Angew Chem, Int 2010, 49, 1726.

- (a) Ri, T.; Eyring, H. J Chem Phys 1940, 8, 433;(b) Walden, P. Angew Chem 1924, 37, 390.
- (a) Cox, E. G.; Jeffery, G. A.; Truter, M. R. Nature 1948, 162, 258; (b) Grison, E.; Ericks, K.; de Vries, J. L. Acta Cryst 1950, 3, 290; (c) Goddard, D. R.; Hughes, E. D.; Ingold, C. K. J Chem Soc 1950, 1, 2559.
- (a) Gillespie, R. J.; Graham, J.; Hughes, E. D.; Ingold, C. K.; Peeling, E. R. Nature 1946, 158, 480; (b) Gillespie, R. J.; Millen, D. J. Q Rev (London) 1948, 2, 277.
- 25. Chedin, J. Ann Chim 1937, 8, 295.
- Olah, G. A.; Kuhn, S. J.; Flood, S. H. J Am Chem Soc 1961, 83, 4581–4585 and references cited there in.
- (a) Ingold, C. K.; Hughes, E. D.; Reed, R. I. Nature 1946, 158, 448; (b) Halberstadt, E. S.; Hughes, E. D.; Ingold, C. K. Nature 1946, 158, 514; (c) Halberstadt, E. S.; Hughes, E. D.; Ingold, C. K. J Chem Soc 1950, 2441.
- Martinsen, H. Z Phys Chem 1904, 50, 385; 1907, 59, 605.
- 29. Kecki, Z. Tetrahedron 1961, 12, 23.
- Miller, R. C.; Noyce, D. S.; Vermeulen, T. Ind Eng Chem 1964, 56, 43.
- 31. Amol, A.; Kulkarni, B. J Org Chem 2014, 10, 405.
- (a) Ramesh, K.; Shylaja, S.; Rajanna, K. C.; Giridhar Reddy, P.; Saiprakash, P. K. Adv Phys Chem 2013, 146585; (b) Int J Chem Kinet 2014, 46, 126.
- Satish Kumar, M.; Rajanna, K. C.; Venkateswarlu, M.; Lakshman Rao, K. Int J Chem Kinet 2016, 48, 171–196.
- Srinivas, P.; Rajanna, K. C.; Satish Kumar, M.; Rajendar Reddy, K. Synth React Inorg Metal-Org Nano-Met Chem 2014, 44, 364.
- (a) Glasstone, S.; Laidier, K. J.; Eyring, H. Theory of Rate Processes; McGraw-Hil: New York, 1961;
 (b) Laidler, K. J. Chemical Kinetics; Pearson Education: Singapore, 2004.
- 36. Christian, R. Solvents and Solvent Effects in Organic Chemistry; Wiley-VCH: Weinheim, Germany, 2003.
- Robinson, R. A.; Stokes, R. H. Electrolyte Solutions; Butterworths Scientific Publications: London, 1955.
- 38. Brown, D. A.; Hudson, R. F. J Chem Soc 1953, 883.
- 39. (a) Amis, E. S. Solvent Effects on Reaction Rates and Mechanisms; Academic Press: London, 1964;
 (b) Kirkwood, J. G. J Chem Phys 1924, 2, 251.
- (a) Ingold, C. K. Structure and Mechanism in Organic Chemistry; Bell: London, 1953; (b) Hughes, E. D.; Ingold, C. K. J Chem Soc 1935, 244.
- Shorter, J. Correlation Analysis in Organic Chemistry: Introduction to Linear Free-energy Relationships; Clarendon Press: Oxford, UK, 1973, pp. 70.
- Basolo, F.; Pearson, R. G. Mechanisms of Inorganic Reactions—A Study of Metal Complexes in Solution, 2nd ed.; Wiley : New York, 1967.
- (a) Hammett, L. P. Physical Organic Chemistry; Mc-Graw-Hill: New York, 1940; (b) Wiberg, K. B. Physical Organic Chemistry; Wiley: New York, 1964.
- 44. Exner, O. Coll Czech Chem Commun 1955, 29, 1094.
- 45. (a) Petersen, J. R. C. J Org Chem 1964, 29, 3133;
 (b) Liu, L.; Guo, Q. X. Chem Rev 2001, 101, 673–693;
 (c) Cornish-Bowden, A. J Biosci 2002, 27, 121–126.