Canadian Chemical Transactions Year 2015 | Volume 3 | Issue 4 | Page 461-472

Research Article

DOI:10.13179/canchemtrans.2015.03.04.0239

Oxidation of *N*,α-diphenylnitrones by *N*-chlorosuccinimide in Alkaline Medium – A Non-linear Hammett Plot

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Received: *October 1, 2015* ***Revised:*** *January 2, 2016* ***Accepted:*** *January 5, 2016* *Published: January 6, 2016*

Abstract: The kinetics of oxidation of some substituted N,a-diphenylnitrones by N-chlorosuccinimide (NCS) to yield benzaldehyde and nitrosobenzene was studied. The reaction follows first order kinetics with respect to [NCS] and fractional order with respect to [nitrone]. The order with respect to alkali was inverse fractional order. The reaction exhibited both negative and positive Hammett reaction constants depending upon the nature of substituents. A plot of rate constant (log *k*) and s gave a concave downward curve. The electron releasing substituents fall on one side of curve and electron withdrawing substituents fall on another side. The activation parameters were calculated. A probable mechanism consistent with experimental observations has been proposed.

Keywords: N,α-diphenylnitrones; N-chlorosuccinimide; Oxidation; Isokinetic plot; Hammett plot

1. INTRODUCTION

N-Chlorosuccinimide (NCS) has been used both as oxidizing and chlorinating agent in organic chemistry [1-6]. Several reports on the kinetics and mechanism of oxidation by NCS are available in the literature [7–13]. An exhaustive survey of literature reveals that only a few reports are available on the kinetic studies on nitrones [14–22]. However, the kinetics of oxidation of nitrones by NCS has not been investigated. In the present article, we report the kinetics of oxidation of some substituted nitrones by NCS in alkaline medium.

2. EXPERIMENTAL

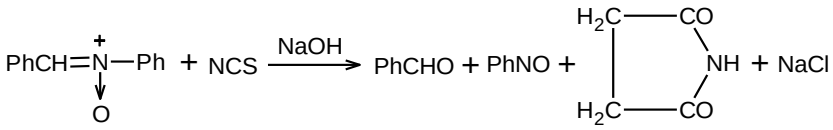
N-Chlorosuccinimide was prepared by passing chlorine gas through a 50% (v/v) aqueous alcoholic solution of succinimide [23]. N,α-diphenylnitrone and substituted nitrones were prepared by the literature methods [24]. AnalaR grade samples of sodium perchlorate, sodium hydroxide, succinimide and acrylonitrile were used. Triply distilled water was used throughout the course of the investigation.

2.1. Kinetic measurements

Reactions were carried out under pseudo-first order conditions keeping an excess of the nitrones over NCS. The reaction solutions containing all constituents were equilibrated in a thermostat and the mixture was monitored for two half lives by iodometric determination of unreacted NCS. The first-order rate constants were determined and the results were reproducible within ± 3%.

2.2. Stoichiometry and product analysis

The stoichiometry was studied under the reaction conditions by keeping excess of NCS was kept for 24 hrs. The estimation of unreacted NCS indicated that one mole of NCS was used by one mole of nitrone.



For identifying the product, an excess of NCS was mixed with nitrone and was kept for 24 hours under kinetic conditions. After this period, the products were extracted with chloroform. The extract was evaporated to remove the solvent and the solid obtained was analysed by TLC method. The residue was purified on a silica gel eluent CCl_4/Et_2O. The spots of the products were developed in benzene along with the spots of authentic samples of benzaldehyde and nitrosobenzene. Two spots were obtained, products were identical with benzaldehyde and nitrosobenzene and the products were also identified by using IR [25].

Table 1. Effect of oxidant and substrate at temperature = 308 K; $[OH^-] = 1.25 \times 10^{-3}$ mol dm^{-3}; acetonitrile-water = 50% (v/v)

[NCS] × 10^3 (mol dm^{-3})	[nitrone] × 10^2 (mol dm^{-3})	k_{obs} × 10^3 (s^{-1})
0.50	1.00	3.54
1.00	1.00	4.44
1.50	1.00	4.52
2.00	1.00	4.44
2.50	1.00	4.67
3.00	1.00	4.67
1.00	0.50	2.82
1.00	0.75	3.48
1.00	1.00	4.44
1.00	1.50	6.44
1.00	2.00	7.36

3. RESULTS AND DISCUSSION

The reaction was first order in NCS as seen from the linearity of log [NCS] *versus* time plots in all the cases. The rate measurements with varying [nitrone] show that the order of nitrone was fractional (Tables 1 and 4). Plot of $1/k_{obs}$ *versus* 1/[nitrone] was linear with finite intercept on rate constant ordinates. This supports the fractional order with respect to [nitrone]. Few substituted nitrones were carried out under same experimental condition shows that nitrones are fractional order with respect to [nitrone] (Table 2).

The rate increased with decrease in $[OH^-]$. The plot of log k_{obs} *versus* log $[OH^-]$ was linear with a negative slope of less than unity, indicating the inverse fractional-order dependence on $[OH^-]$ (Table 3). The ionic strength of the reaction solution was varied from 0.01125 to 0.0625 mol dm^{-3} with sodium perchlorate at fixed concentration of other reactants. The rate increases with increase in concentration of $NaClO_4$ (Table 2).

Table 2. Kinetic data for the oxidation of some substituted nitrones by N-chlorosuccinimide in aqueous-alkaline: $[OH^-] = 1.25 \times 10^{-3}$ mol dm^{-3}, $[NaClO_4] = 2.5 \times 10^{-3}$ mol dm^{-3}, $[NCS] = 1.00 \times 10^{-3}$ mol dm^{-3}, acetonitrile-water = 50% (v/v), temperature = 308 K

Substituents	[Substrate] × 10^2 (mol dm^{-3})	$k_{obs} \times 10^3$ (s^{-1})	Order
p-OMe	0.53	1.05	0.810
	1.06	2.54	
	1.60	2.84	
	2.10	3.24	
p-Me	0.57	1.08	0.652
	1.14	1.43	
	1.72	2.08	
	2.34	2.72	
p-Br	0.44	1.52	0.560
	0.72	2.25	
	1.30	3.10	
	1.84	3.36	
p-NO_2	0.50	2.20	0.604
	1.12	3.06	
	1.52	4.44	
	2.10	5.12	

Table 3. Effect of varying of [OH^-] and [$NaClO_4$]: [NCS] = 1.00×10^{-3} mol dm^{-3}, [nitrone] = 1.00×10^{-2} mol dm^{-3}, acetonitrile-water = 50% (v/v), temperature = 308 K

$[OH^-] \times 10^3$ (mol dm^{-3})	$[NaClO_4] \times 10^{-1}$ (mol dm^{-3})	$k_{obs} \times 10^3$ (s^{-1})
1.25	5.00	4.44
2.50	5.00	3.54
3.75	5.00	3.13
5.00	5.00	2.53
6.25	5.00	2.33
7.50	5.00	2.00
1.25	1.25	2.93
1.25	2.50	3.31
1.25	3.75	4.00
1.25	5.00	5.31
1.25	6.25	7.55

Table 4. Effect of varying [SA] and [Br^-]: [NCS] = 1.00×10^{-3} mol dm^{-3}, [nitrone] = 1.00×10^{-2} mol dm^{-3}, [OH^-] = 1.25×10^{-3} mol dm^{-3}, acetonitrile-water = 50% (v/v), temperature = 308 K

[Succinimide] $\times 10^2$ (mol dm^{-3})	$[Cl^-] \times 10^{-3}$ (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})
0.50	–	4.48
1.00	–	4.40
1.50	–	4.12
2.00	–	4.38
2.50	–	4.49
3.00	–	4.31
–	0.50	7.00
–	1.00	7.64
–	1.50	9.64

–	2.00	10.88
–	2.50	12.48
–	3.00	13.02

The effect of the product succinimide has been studied by varying the [succinimide] at a given substrate concentration (Table 4). The reaction rate did not alter, indicating the absence of this compound in a pre-equilibrium to the rate limiting step.

The influence of dielectric constant (ε) of the medium on the rate of reaction was studied in binary solvent mixtures of acetonitrile and water. With increasing acetonitrile content (decreasing ε) of the medium the rate of the reaction decreased and values are summarised in Table 5. The plot of log k_{obs} *versus* (ε−1/ε+1) is linear with a positive slope, indicating dipole-dipole type of reaction [26]. A free radical mechanism was ruled out due to the absence of polymerisation of acrylonitrile when added to the reaction mixture.

Table 5. Effect of solvent composition on the reaction rate: [nitrone] = 1.00×10^{-2} mol dm^{-3}, [NCS] = 1.0×10^{-3} mol dm^{-3}, [OH^-] = 1.25×10^{-3} mol dm^{-3}, [$NaClO_4$] = 5.0×10^{-3} mol dm^{-3}, temperature = 308 ± 0.1 K

% AN (v/v)	$k_{obs} \times 10^4$ (s^{-1})
50	4.44
55	4.30
60	4.13
65	3.82
70	3.52
75	3.15
80	2.77

3.1. Mechanism and rate law

The reaction is first order in [NCS], fractional order in [nitrone] and inverse fractional order in [OH^-] which can be accounted for by the Schemes 1 and 2. In alkaline solutions, it is likely that NCS also exist as OCl^-.

$$OCl^- + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} HOCl + OH^- \quad (1)$$

$$HOCl \xrightarrow{k_2} Cl^+ + OH^- \text{ (slow)} \quad (2)$$

$$S + Cl^+ \xrightarrow{k_3} SCl^+ \text{ (fast)} \quad (3)$$

$$SCl^{+} + Cl^{-} + H_2O \xrightarrow{k_4} \text{final product (fast)} \quad (4)$$

where S = substrate (nitrone)

Application of steady state principle to the intermediate HOCl in **Scheme 1** leads to the rate law (5)

$$\frac{-d[NCS]}{dt} = \frac{K_1 k_2 [H_2O][NCS]_0}{[OH^-] + K_1[H_2O]} \quad (5)$$

Scheme 1

$$NCl + S \xrightarrow{k_5} N^{-} + SCl^{+} \text{ (slow)} \quad (6)$$

$$N^{-} + H_2O \xrightarrow{k_6} NH + OH^{-} \text{ (fast)} \quad (7)$$

$$SCl^{+} + NCl + H_2O \xrightarrow{k_6} \text{final products (fast)} \quad (8)$$

where [S] = [nitrone]

The rate law in accordance with above mechanism is given by equation (9)

$$\frac{-d[NCS]}{dt} = k_5 [NCS]_0 [S] \quad (9)$$

equation (10) or (11) gives the combined rate law

$$\frac{-d[NCS]}{dt} = \frac{K_1 k_2 [H_2O][NCS]_0}{[OH^-] + K_1[H_2O]} + k_5 [NCS]_0 [S] \quad (10)$$

$$k_{obs} = \frac{K_1 k_2 [H_2O]}{[OH^-] + K_1[H_2O]} + k_5 [S] \quad (11)$$

Plot of k_{obs} *versus* [S] is linear in conformity with rate law (11)

Further, equation (11) can be rearranged as

$$(k_{obs} - k_5[S]) = \frac{K_1 k_2 [H_2O]}{[OH^-] + K_1[H_2O]} \quad (12)$$

$$\frac{1}{(k_{obs} - k_5 [S])} = \frac{[OH^-]}{K_1 k_2 [H_2O]} + \frac{1}{k_2} \quad (13)$$

Scheme 2

Plot of $\frac{1}{(k_{obs} - k_5 [S])}$ *versus* [OH^-] was linear in accordance with rate raw (13) providing an additional support for the proposed mechanism.

3.2. Effect of substituents on reaction rate

The rate constants of some *meta*- and *para*-substituted N,α-diphenylnitrones were measured at four different temperature. The thermodynamic parameters were evaluated and the second order rate constants (k_2) are listed in Table 6.

Table 6. Second order rate constants and activation parameters for the oxidation of nitrones by NCS: [NCS] = 1.00×10^{-3} mol dm^{-3}, [OH^-] = 1.25×10^{-3} mol dm^{-3}, [nitrone] = 1.00×10^{-2} mol dm^{-3}, acetonitrile-water = 50% (v/v)], [$NaClO_4$] = 5.0×10^{-3} mol dm^{-3}

S. No.	X =	$k_2 \times 10^2$ (dm^{-3} mol^{-1} s^{-1})				$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J K^{-1} mol^{-1})	$^*\Delta G^{\#}$ (kJ mol^{-1})	R	sd
		298 K	303 K	308 K	313 K					
1.	H	2.00	3.60	4.44	5.81	50.49	107.25	83.52	0.971	0.125
2.	*p*-Me	1.67	2.16	3.13	3.24	34.16	164.10	85.25	0.960	0.102
3.	*p*-OMe	1.36	1.66	2.39	2.76	36.06	159.72	84.52	0.985	0.062
4.	*p*-F	1.64	2.57	2.91	3.74	37.84	151.57	83.00	0.970	0.096
5.	*p*-Cl	1.51	1.89	2.87	3.23	39.36	141.72	85.03	0.978	0.084
6.	*p*-Br	1.50	1.86	2.57	3.01	34.90	162.75	86.29	0.991	0.045
7.	*p*-NO_2	1.00	1.22	1.40	1.90	29.40	184.71	84.55	0.983	0.055
8.	*m*-F	1.44	1.80	2.34	2.75	31.66	173.92	85.23	0.976	0.027
9.	*m*-Cl	1.37	1.75	2.01	2.30	23.77	200.61	85.52	0.987	0.038
10.	*m*-Br	1.34	1.70	2.07	2.34	26.50	191.64	85.54	0.990	0.037
11.	*m*-NO_2	1.26	1.31	1.65	2.06	23.81	201.86	85.98	0.955	0.075

The low energy of activation and high free energy of activation ($\Delta G^{\#}$ at 308 K) support the formation of highly solvated transition state. A large negative entropy of activation suggests the formation of composite activated complex with few degrees of freedom [26,27].

A plot of $\Delta H^{\#}$ *versus* $\Delta S^{\#}$ gives a straight line with good correlation [27] (Figure 1). The value of isokinetic temperature from the plot was 297 K, which is less than the experimental temperature indicating the reaction is under entropy control.

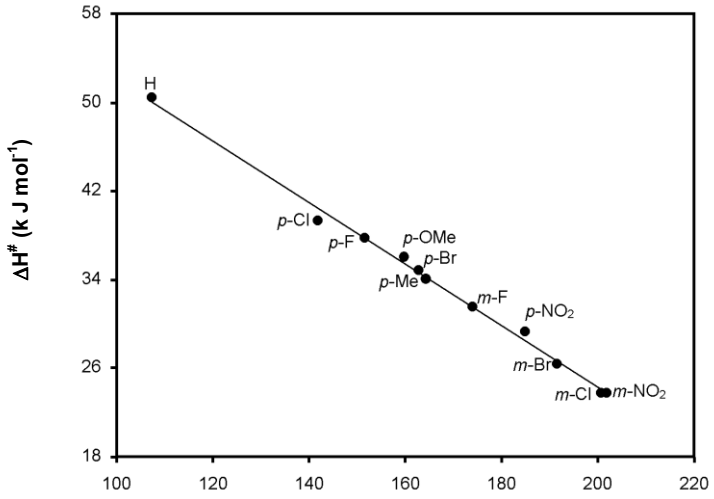


Figure 1. Plot of $\Delta H^{\#}$ *versus* $-\Delta S^{\#}$ for oxidation of nitrogen by NCS

The Exner's plot of log $k_{2(313\ K)}$ *versus* log $k_{2(298\ K)}$ (Figure 2) was drawn and the value of β calculated from the relation $\beta = T_1T_2\ (1\text{-}b)/(T_2b\text{-}T_1)$ is in good agreement with that calculated from isokinetic plot. Since the β value is less than experimental temperature it also indicates an entropy controlled reaction. Constancy of $\Delta G^{\#}$ values calculated for all the nitrones indicates that probably the same mechanism operates in all the cases.

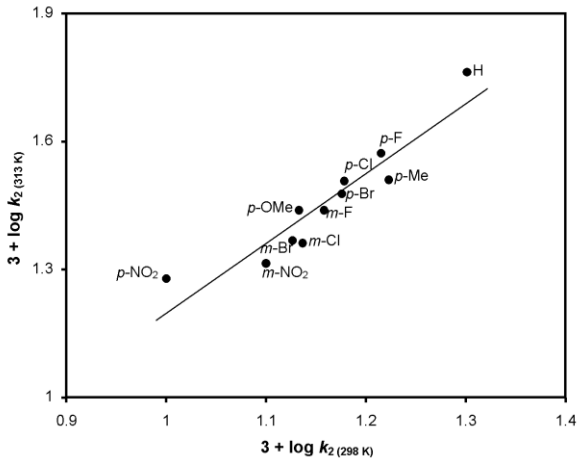


Figure 2. Exner plot for oxidation of nitrones by NCS

The Hammett equation applied with the usual substituent constant σ values and log k_2 data on *meta*- and *para*-substituted nitrones exhibited a concave downward curve (Figure 3). Similar types of reactions have been reported earlier [28–36].

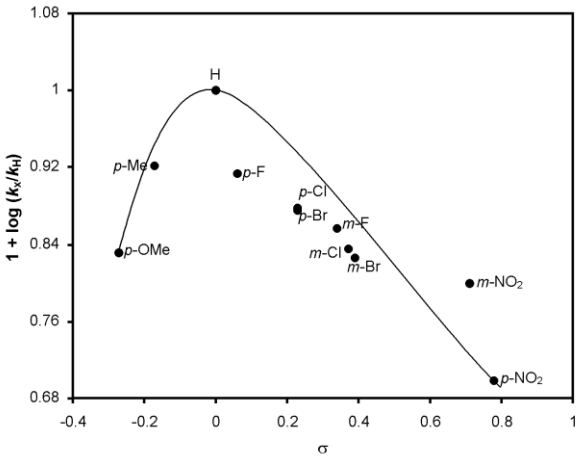


Figure 3. Hammett plot for oxidation of nitrones by NCS

The electron releasing substituents fall on one side of the curve with a negative slope and the electron-withdrawing substituents on the other side with positive slope. The values of ρ+ and ρ- at different temperatures are given in Table 7.

Table 7. Reaction constants for the oxidation of nitrones by N-chlorosuccinimide

Temperature	ρ^+	r	ρ^-	r
298	0.262	0.998	0.134	0.948
303	0.493	0.976	0.223	0.900
308	0.413	0.984	0.240	0.953
313	0.331	0.953	0.228	0.840

Both electron releasing and withdrawing groups decreased the rate compared to the parent compound. The reason for the break in the Hammett plot is a change in the reaction mechanism. A change in the rate-determining step with change in the nature of the substituents and a change in the transition state.

In this reaction kinetics, the non-linear Hammett plot, is not due to change in the reaction mechanism with respect to substituents. Because, the isokinetic plot and Exner's plot gave good correlation and the non-linear Hammett plot is only due to a change in the transition state [28, 29, 31, 32, 37,38].

4. CONCLUSION

Oxidation of nitrones by NCS were carried out in alkaline medium. The order with respect to substrate fractional order and inverse fractional order with respect to alkaline. A concave downward Hammett plot is obtained, all the substituents follow a common mechanism because of constancy of free

energy of activation. The isokinetic temperature β is less than that of reaction temperature which implies that oxidation reaction is entropy controlled. All the substituents follow a common mechanism.

REFERENCES

[1] Franc¸ois Munyemana; Isabelle George; Alain Devos; Alain Colens; Eduard Badarau; Anne-Marie Frisque-Hesbain; Aurore Loudet; Edmond Differding; Jean-Marie Damien,Jeanine Rémion; Jacqueline Van Uytbergen, Léon Ghosez, A mild method for the replacement of a hydroxyl group by halogen. 1. Scope and chemoselectivity. *Tetrahedron*, **2016,** 72, 420-430.

[2] Bryant Catano; John Lee; Claudia Kim; David Farrell; Jeffrey L. Petersen; Yalan Xing. Iron(III) catalyzed halo-functionalization of alkynes, Tetrahedron Lett., **2015**, 56, 4124–4127.

[3] Anitha Devi, R.; Deivanayagam Easwaramoorthy, D.; Ravichandran, C. Oxidation of 3 -Carboxy-3-Hydroxy Pentane dioic Acid by N-Chlorosuccinimide in alkaline medium – kinetics and mechanism, *Int.J. ChemTech Res*. **2015**,8(5), 175-182.

[4] Liu, Y.C.; LEE, C.F. *N*-Chlorosuccinimide-promoted synthesis of thiophosphates from thiols and phosphonates under mild conditions. *Green Chem.* **2014**, *16***,** 357-364.

[5] Candy, M.; Guyon, C.; Mersmann, S.; Chen, J.R.; Bolm, C. Synthesis of sulfondiimines by *N*-chlorosuccinimide-mediated oxidative imination of sulfiliminium salts. *Angew Chem Int Ed.* **2012**, *51*, 4440-4443.

[6] Srinivasan, S.; Venkatasubramanian, N. Oxidation of alcohols by N-chlorosuccinimide-A kinetic study. *Tetrahedron*, **1974**, *30*, 419-425.

[7] Thimme Gowda, B.; Ishwara Bhatt, J. Kinetics of oxidation of thiocyanate ion by N-Chloro and N-Bromosuccinmides in aqueous methanol and alkaline media. *Indian J Chem A*, **1989**, *28*, 43.

[8] Dikshitulu, L.S.A.; Rao, V.H.; Kumar, B.V. *Natl Acad Sci Lett India*, **1984**, *7*, 115.

[9] Tikhonova, G.P.; Bovkovets, S. *Russ J Inorg Chem*, **1978**, *23*, 1687.

[10] Halligudi, N.N.; Desai, S.M.; Nandibewoor, S.T. Kinetics and mechanism of palladium(II) catalysed oxidation of allyl alcohol by N-Chloro succinimide in aqueous alkaline medium. *Ind J Chem A*, **1999**, *38*, 943-946.

[11] Thenraja, D.; Subramanian, P.; Srinivasan, C. Kinetics and mechanism of oxidation of aromatic sulfides and arylmercaptoacetic acids by *N*-Chlorosuccinimide. *J Chem Soc Perkin Trans*, **2002**, *2*, 2125-2129.

[12] Matsuo, J.; Iida, D.; Yamanaka, H.; Mukaiyama, T. *N*-tert-Butylbenzenesulfenamide- catalyzed oxidation of alcohols to the corresponding carbonyl compounds with *N*-Chlorosuccinimide. *Tetrahedron*, **2003**, *59*, 6739-6750.

[13] Singh, A.K.; Yadav, S.; Srivastava, R.; Srivastava, J.; Rahmani, S. Kinetic and mechanistic investigation of Pd(II)-catalysed and Hg(II)-co-catalysed oxidation of D(+)melibiose by *N*-Bromoacetamide in acidic medium. *J Organomet Chem*, **2010**, *695*, 2213-2219.

[14] Han, C.S.; Lee, K.W.; Jaffe, H.H. Wallach Rearrangement. II. Kinetics of the rearrangement of azoxybenzene and its derivatives in strongly acidic solution. *J Am Chem Soc*, **1967**, *89*, 4975-4981.

[15] Bluhm, A.L., Weinstein, J. Stable radicals by photooxidation of nitrones. *J Am Chem Soc*, **1970**, *92*, 1444-1445.

[16] Uma, M.; Gopalakrishnan, M.; Jayabharathi, J.; Thanikachalam, V. Kinetics of oxidation of some substituted N,α–diphenyl nitrones by bromamine-B in the presence of acid medium. *Indian J Chem B*, **1995**, *34*, 612-616.

[17] Uma, M.; Gopalakrishnan, M.; Jayabharathi, J.; Thanikachalam, V. Kinetics of oxidation of some substituted N,□-diphenylnitrone by Bromamine-B in acidic medium. *J Ind Chem Soc*, **1996**, *73*, 329-334.

[18] Gopalakrishnan, M.; Jayabharathi, J.; Thanikachalam, V. Separation of electronic and steric effects: oxidation of ortho-substituted N,α-Diphenylnitrones by pyridinium fluorochromate in aqueous DMF medium. *Asian J Chem*, **1999**, *11*, 1459.

[19] Gopalakrishnan, M.; Uma, M.; Jayabharathi, J.; Thanikachalam, V. Kinetics of oxidation of N,□-diphenyl nitrones by pyridinium fluorochromate in aqueous DMF medium. *Afinidad*, **2002**, *59*, 688-672.

[20] Gopalakrishnan, M.; Jayabharathi, J.; Uma, M.; Thanikachalam, V. Oxidation of N, α-Diphenylnitrones by pyridinium chlorochromate in aqueous DMF medium. A Kinetic Study. *Oxid Commun*, **2007**, *30*, 625-632.

[21] Manivarman, S.; Manikandan, G.; Jayabharathi, J.; Sekar, M.; Thanikachalam, V. Kinetics and mechanism of oxidation of some substituted nitrones by N-Bromosuccinimide in aqueous alkaline medium. A kinetic study. Oxid Commun, **2007**, *30*, 823-831; Mechanistic investigation of N,α-Diphenylnitrones oxidation by N-bromosuccinimide.
Non-linear Hammett Plot. *Oxid. Commun.*, **2007**, *30*, 832-841.

[22] Rajarajan, G.; Jayachandramani, N.; Manivarman, S.; Jayabharathi, J.; Thanikachalam, V. Kinetics and mechanism of oxidation of *N*,α-Diphenylnitrones by 4-(dimethylamino) pyridinium chlorochromate (DMAPCC) in aqueous DMF medium. *Transit Met Chem*, **2008**, *33*, 393-397.

[23] Perin, D.D.; Armarego, W.L.F. Purification of laboratory chemicals, 3rd edn. (Pergamon Press, Oxford) **1998**.

[24] Vogel, A.I. A textbook of practical organic chemistry, 5th edn. (Longmanns, London) **1989**, 955.

[25] Bradley, G.M.; Strauss, H.L. Infrared studies of nitrosobenzene. *J Phys Chem*, **1953**, *79*, 1953-1957.

[26] Hammett, L.P. Physical organic chemistry (McGraw-Hill, New York) **1940**, 193.

[27] Leffler, J.E. The enthalpy-entropy relationship and its implications for organic chemistry. *J Org Chem*, **1955**, *20*, 1202-1231.

[28] Burnett, J.F.; Zahler, R.E. Aromatic nucleophilic substitution reactions. *Chem Rev*, **1951**, *49*, 273-412.

[29] Swain, C.G.; Langsdorf, W.P. Concerted displacement reactions. VI. *m*-and *p*-substituent effects as evidence for a unity of mechanism in organic halide reactions. *J Am Chem Soc*, **1951**, *73*, 2813-2819.

[30] Noyce, D.; Bottini, A.; Smith, S. Notes-Carbonyl Reactions. III. The formation of aromatic semicarbazones. A nonlinear rho-sigma correlation. *J Org Chem*, **1958,** *23*, 752-753.

[31] Anderson, B.M.; Jencks, W.P. The effect of structure on reactivity in semicarbazone formation. *J Am Chem Soc*, **1960**, *82*, 1773-1777.

[32] Pratt, E.F.; Kamlet, M.J. Reaction rates by distillation. X. The condensation of anilines with benzoins. *J Org Chem*, **1963**, *28*, 1366-1368.

[33] Fuchs, R.; Carlton, D.M. Multiple Substituent effects in the solvolysis and thiosulfate reactions of 4-substituted α-chloro-3-nitrotoluenes. *J Org Chem*, **1962**, *27*, 1520-1523.

[34] Fuchs, R.; Carlton, D.M. Substituent effects in the solvolysis and thiosulfate reactions of 3-, 4- and 3,5-substituted α-chlorotoluenes. *J Am Chem Soc*, **1963**, *85*, 104-107.

[35] Beltrame, P.; Veglio, C.; Simonetta, M. Kinetics of the reaction of a substituted benzonitrile oxide with some arylacetylenes. *Chem Commun* (London), **1966**, 433-434.

[36] Hoffmann, J.; Klicnar, J.; Sterba, V.; Vecera, M. Kinetics of hydrolysis of substituted salicylideneanilines. *Collect Czech Chem Commun*, **1970**, *35*, 1387-1398.

[37] Sabapathymohan, R.T.; Gopalakrishnan, M.; Sekar, M. Kinetics and mechanism of oxidation of some substituted trans-cinnamic acids by pyridinium chlorochromate - A non-linear Hammett plot. *Tetrahedron*, **1994**, *50*, 10933-10944.

[38] Meenakshisundaram, SP.; Amutha, M. Studies on the oxidation of some sulfides with pyridinium dichromate in acetonitrile medium. *J Chem Res. (S)* **1999**, 2-3.

The authors declare no conflict of interest

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