Global Journals Inc.
GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH: B
CHEMISTRY
Volume 15 Issue 4 Version 1.0 Year 2015
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

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*GJSFR-B Classification : FOR Code: 030703*

# Studies on the Kinetics and Mechanism of Oxidation of Nitrones by Pyrazolinium Dichromate in Aqueous DMSO Medium

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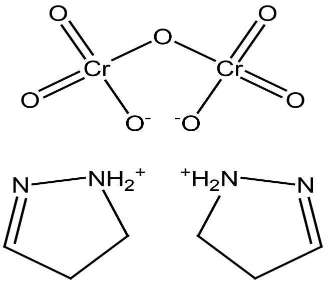
*Keywords: N, α- diphenylnitrones, pyrazolinium dichromate, kinetics, isokinetic plot, entropy, enthalpy and rate constants.*

## I. Introduction

The kinetics and oxidation of mono substituted N,α-diphenylnitronesby Pyrazolinium dichromateto yield the corresponding aldehyde and nitrosobenzene have been studied. The reaction is first order with respect to the nitrone and PyDC. The reaction is negative reaction constants. The reaction is catalysed by the acid and the order with respect to acid is fractional. The effect of temperature, solvent composition and oxalic acid were studied and activation parameters are evaluated. Probable mechanism was discussed.

The kinetics and mechanistic studies of oxidation of great variety of organic compounds by PyDC [1-2]. There is no indication of any unusual effectiveness, utility, or advantage to be gained by the use of pyridinium dichromate as a discrete oxidizing species [3]. The kinetics of oxidation of nitrones as a substrate is reported earlier [4-8]. The present paper describes the kinetics of oxidation of nitrones by Pyrazolinium dichromatein aqueous dimethyl sulphoxidemedium evaluate the reaction constants and the mechanistic aspects are discussed.

The structural formula of PyDC is shown in the following figure.



PYRAZOLINIUM DICHROMATE

$[C_6H_{14}N_4]Cr_2O_7$

## II. Materials and Methods

Pyrazolinium dichromate(PyDC) was prepared by reported method [1], nitrones and substituted nitrones were prepared by the literature method[9], purified acrylamide[10] analar sample of sodium perchlorate, perchloric acid, oxalic acid, manganoussulphate and ethylene diamine tetra aceticacid were used. Triply distilled water was used throughout the course of the investigation. Correlation analysis werecarried out using Microcal Origin (Version 6.1) computer software.

### a) *Preparation of Pyrazolinium dichromate*

Chromium trioxide (5g) was dissolved in water (50 ml) and cooled in ice. Then pyrazole (4g) was added, slowly. The solution was diluted with acetone (200 ml) and cooled to 0°C. The orange solid obtained was separated, filtered, washed with acetone, dried and recrystallized from water (dec.160°-161°C).

### b) *Kinetic measurements*

For kinetic runs, a measured amount of PyDC pre-equilibrated at 30°C was rapidly added to the thermally equilibrated mixture containing appropriate amounts of nitrones, acrylamide, perchloric acid, sodium perchlorate and water. The progress of the reaction was followed by iodometric determination of the

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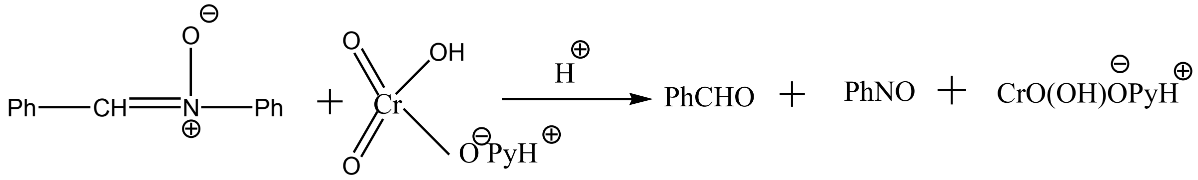
unreacted oxidant[11]. The rate constants were determined by the least squares method. Aliquots (2 ml) of reaction mixture were withdrawn at an appropriate time interval and quenched into ice-cold water containing 10 ml of 4N sulphuric acid. The liberated iodine was titrated against standard sodium thiosulphate to a starch end point. The reaction was carried out at three different temperatures viz., $35^0$, $40^0$ and $45^0$C.

### c) *Stoichiometry and Product analysis*

The reaction mixture containing excess of PyDC in the presence of perchloric acid was kept for 24hr under kinetic conditions. The estimation of unreacted PyDC indicates that 1mol of PyDC was used by 1mol of nitrone.



For identifying the product an excess of oxidant was mixed with substrate under kinetic conditions. After the reaction was completed, the reaction mixture was extracted with chloroform. The solvent was removed and obtained solid was analysed by Co-TLC method. The spots of the products were developed in benzene along with the spots of authentic samples of benzaldehyde and nitrosobenzene. After developing the location of the spots was identified using iodine vapour and their positions were compared. Two spots obtained for products were identical with benzaldehyde and nitrosobenzene. IR spectrum was recorded, nitrosobenzene [12] exhibits three bands at 1626, 1500 and 1019cm$^{-1}$ attributed to stretching frequency of C-N, one sharp band at 1452cm$^{-1}$ due to stretching vibration of N-O and band 530cm$^{-1}$ due to ring deformation and CNO bending vibration are similar to that of one of product obtained from the substrate.

## III. Results and Discussion

An inspection of the observed Pseudo-first-order rate constants ($k_{obs}$) shows that the $k_{obs}$values constant over a wide range in PyDC(Table-1). The reaction is first order with respect to PyDC as evidenced by a good linearity in the plot of log[PyDC] versus time. The plot of log$k_{obs}$ versus log[NO] was found to be linear(Table-1) with slope unity, indicating a first order dependence on [NO]. The plot of $k_{obs}^{-1}$ versus $[NO]^{-1}$ was linear and passing through the origin, showing that the nitrone-PyDC complex has only transient existence. The effect of acid[$HClO_4$] has been studied by varying the concentration of $H^+$ at a given concentration(Table-1). The plot of $k_{obs}$ versus log[$H^+$] was linear with a slope less than unity, indicating fractional order dependence on [$H^+$]. The rate decreased with increase in ionic strength of the medium by the addition of $NaClO_4$ (Table-1).

*Table 1 :* Effect of varying [PyDC], [Nitrone], [$H^+$] and [$NaClO_4$] on oxidation of nitrone in 50 % (v/v) DMSO – $H_2O$ medium at 308 K

| [PyDC] x $10^3$mol dm$^{-3}$ | [Nitrone] x $10^2$mol dm$^{-3}$ | [$HClO_4$] x $10^3$mol dm$^{-3}$ | [$NaClO_4$] x $10^1$mol dm$^{-3}$ | $k_{obs}$ x $10^4$ s$^{-1}$ |
|---|---|---|---|---|
| 0.50 | 1.00 | 1.53 | 1.00 | 8.44 |
| 0.75 | 1.00 | 1.53 | 1.00 | 8.28 |
| 1.00 | 1.00 | 1.53 | 1.00 | 8.01 |
| 1.25 | 1.00 | 1.53 | 1.00 | 8.17 |
| 1.50 | 1.00 | 1.53 | 1.00 | 8.71 |
| 1.75 | 1.00 | 1.53 | 1.00 | 8.61 |
| 1.00 | 0.50 | 1.53 | 1.00 | 4.01 |
| 1.00 | 0.75 | 1.53 | 1.00 | 6.05 |
| 1.00 | 1.00 | 1.53 | 1.00 | 8.01 |
| 1.00 | 1.25 | 1.53 | 1.00 | 10.19 |
| 1.00 | 1.50 | 1.53 | 1.00 | 11.6 |
| 1.00 | 1.75 | 1.53 | 1.00 | 13.1 |
| 1.00 | 1.00 | 0.76 | 1.00 | 5.77 |
| 1.00 | 1.00 | 1.53 | 1.00 | 8.01[a] |
| 1.00 | 1.00 | 2.29 | 1.00 | 8.91 |
| 1.00 | 1.00 | 3.06 | 1.00 | 11.4 |
| 1.00 | 1.00 | 3.82 | 1.00 | 12.9 |
| 1.00 | 1.00 | 4.59 | 1.00 | 15.2 |
| 1.00 | 1.00 | 1.53 | 0.50 | 9.08 |

| | | | | |
|---|---|---|---|---|
| 1.00 | 1.00 | 1.53 | 1.00 | 8.00 |
| 1.00 | 1.00 | 1.53 | 1.50 | 6.23 |
| 1.00 | 1.00 | 1.53 | 2.00 | 3.67 |
| 1.00 | 1.00 | 1.53 | 2.50 | 2.47 |
| 1.00 | 1.00 | 1.53 | 3.00 | 1.41 |

*[Acrylamide] = 1.00 x $10^{-2}$mol $dm^{-3}$*

The reaction is studied on addition of manganous ions reduces [13-15] the rate of oxidation of nitrones. This indicates that Mn(II) has a catalytic effect on the disproportionation of the intermediate valence state of chromium [16] and suggest that Cr(IV) is probably involved in the rate determining step(Table-2). The rate increase with increase in oxalic acid, indicating that oxalic acid enhances the rate of oxidation of aldonitrones by PyDC(Table-2). The increase in [EDTA] [17] inhibits the rate of oxidation of nitrones(Table-2), indicate that complex formation between chromate and PyDC.

*Table 2 :* Effect of varying [ $Mn^{2+}$], [EDTA], [$(COOH)_2$] on oxidation of nitrone by PyDC in 50 % (v/v) DMSO – $H_2O$ medium at 308 K

| [$MnSO_4$] x $10^3$mol $dm^{-3}$ | $k_{obs}$ x $10^4$ $s^{-1}$ | [EDTA] x $10^3$mol $dm^{-3}$ | $k_{obs}$ x $10^4$ $s^{-1}$ | [$(COOH)_2$] x $10^3$mol $dm^{-3}$ | $k_{obs}$ x $10^4$ $s^{-1}$ |
|---|---|---|---|---|---|
| 0.00 | 8.01 | 0.00 | 8.01 | 0.00 | 8.01 |
| 2.50 | 4.82 | 2.00 | 6.18 | 0.75 | 8.10 |
| 5.00 | 4.58 | 4.50 | 6.12 | 2.00 | 8.25 |
| 7.50 | 4.24 | 7.00 | 5.90 | 3.25 | 10.24 |
| 10.00 | 3.65 | 9.50 | 5.74 | 4.50 | 10.80 |
| 12.50 | 3.51 | 12.00 | 5.60 | 5.75 | 11.60 |
| 15.00 | 3.24 | 14.50 | 5.52 | 7.00 | 15.20 |

*[Nitrone] = 1.00 x $10^{-2}$ mol $dm^{-3}$ ; [$HClO_4$] = 15.30 x $10^{-4}$ mol $dm^{-3}$*

*[PyDC] = 1.00 x $10^{-3}$ mol $dm^{-3}$ ; [$NaClO_4$] = 1.00 x $10^{-1}$ mol $dm^{-3}$*

An increase in dimethyl sulphoxide content retarded the reaction rate (Table-3). A plot of log$k_{obs}$ versus $D^{-1}$ (where D is the dielectric constant of the medium) was linear with a negative slope indicative of a dipole interaction in the transition. It shows that positive and neutral molecules interact in the rate determining step [18]. No turbidity has been noticed when a clear reaction mixture was allowed to stand with a drop of acrylonitrile ruling out a free radical mechanism.

*Table 3 :* Effect of varying composition of DMSO on oxidation of nitrone by PyDC at 308 K

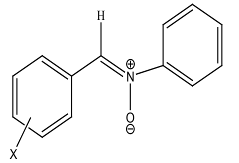
| D | $k_{obs}$ x $10^4 s^{-1}$ | log $k_{obs}$ | $D^{-1}$ |
|---|---|---|---|
| 65.98 | 6.42 | -3.193 | 0.0151 |
| 64.44 | 6.78 | -3.169 | 0.0155 |
| 62.90 | 8.01 | -3.096 | 0.0158 |
| 61.36 | 8.68 | -3.062 | 0.0162 |
| 59.82 | 10.44 | -2.981 | 0.0167 |
| 58.28 | 11.55 | -2.937 | 0.0171 |

*[Nitrone] =1.00 x $10^{-2}$ mol $dm^{-3}$; [$HClO_4$]= 15.30 x $10^{-4}$ mol $dm^{-3}$*

*[PyDC]=1.00 x $10^{-3}$mol $dm^{-3}$ ; [$NaClO_4$] =1.00x $10^{-1}$ mol $dm^{-3}$*

The rate of oxidation of some para and meta-substituted nitrones was studied at three different temperatures, Viz, 35, 40 and 45$^0$C. The activation parameters are calculated using the Eyring's plot and the values are given in (Table-4).

*Table 4 :* Second order rate constants and the activation parameters for the oxidation of substituted nitrones by PyDC

| S.No |  | $k_2$ x $10^2$ $dm^3mol^{-1}$ $s^{-1}$ | | | ΔH$^{\#}$ kJ $mol^{-1}$ | -ΔS$^{\#}$ J $K^{-1}$ $mol^{-1}$ | $^a$ΔG$^{\#}$ kJ $mol^{-1}$ | r | sd |
|---|---|---|---|---|---|---|---|---|---|
| | X | 308 K | 313 K | 318K | | | | | |
| 1 | *p*-OMe | 10.71 | 15.77 | 22.96 | 62.126 | 62.192 | 81.592 | 1.000 | 0.003 |

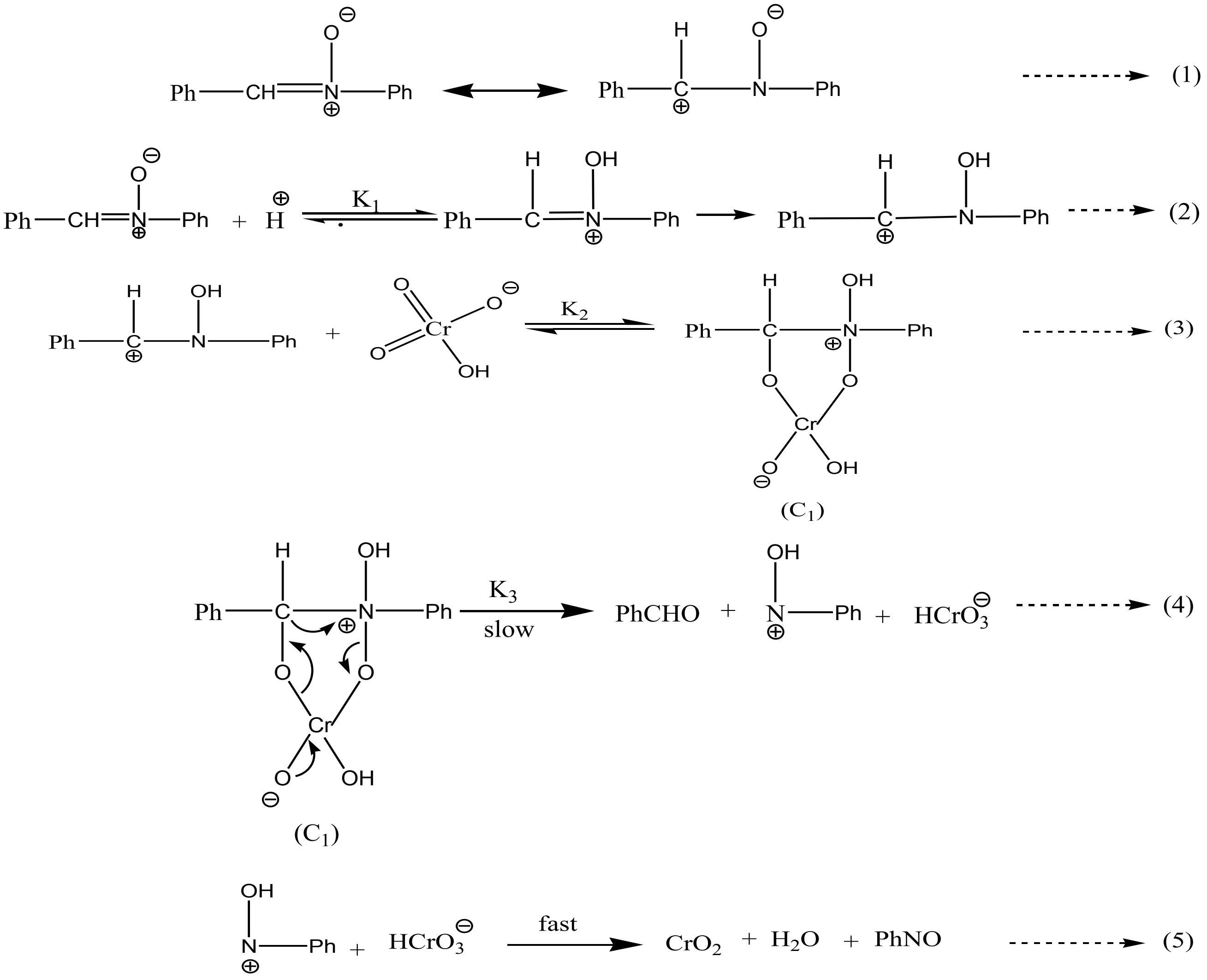
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2 | *p*-Me | 9.67 | 14.38 | 20.69 | 61.976 | 63.522 | 81.859 | 0.999 | 0.008 |
| 3 | H | 8.01 | 12.11 | 18.16 | 64.080 | 58.226 | 82.305 | 0.999 | 0.001 |
| 4 | *p*-F | 7.64 | 10.94 | 15.77 | 59.033 | 75.078 | 82.533 | 0.999 | 0.007 |
| 5 | *p*-Cl | 7.21 | 10.62 | 15.02 | 59.803 | 73.000 | 82.653 | 0.999 | 0.011 |
| 6 | *p*-Br | 6.70 | 10.58 | 13.64 | 57.999 | 79.235 | 82.800 | 0.988 | 0.078 |
| 7 | *p*-$NO_2$ | 4.92 | 06.82 | 10.62 | 62.629 | 67.180 | 83.657 | 0.995 | 0.052 |

*[Nitrone] =* $1.00 \times 10^{-2}$ *mol dm*$^{-3}$*;[NaClO*$_4$*] =*$1.00 \times 10^{-1}$ *mol dm*$^{-3}$*;[HClO*$_4$*] =* $15.30 \times 10^{-4}$*moldm*$^{-3}$*;*
*[PyDC]=* $1.00 \times 10^{-3}$ *mol dm*$^{-3}$*; DMSO – H*$_2$*O = 50 % (v/v) ;* $^a\Delta G^{\#}$ *at 313 K*

*a) Mechanism and rate law*

In aqueous solution PyDC undergo protonation in acidic conditions. This protonated species is more powerful than unprotonated species. The order with respect to PyDC, [NO] is unity and fractional order with respect to [H$^+$]. The PyDC does not undergo protonation at very low [H$^+$].The observed salt and solvent effects show that the ionic and neutral species are involved in the slow step. Owing to the above reasons, the nitrone gets protonated before the rate determining step, and it can react with PyDC in the slow step.

Based on the above observation, a probable mechanism and rate law for the oxidation of nitrones by PyDC given in the following Scheme.



$$Cr\,(IV) + Mn\,(II) \longrightarrow Cr\,(III) + Mn\,(III) \quad \dashrightarrow (6)$$

$$Rate = K_3\,[C_1] \quad \dashrightarrow (7)$$

*Scheme*

$$\frac{-d[PyDC]}{dt} = \frac{K_1 K_2 K_3 [nitrone] [PyDC] [H^+]}{1 + K_1 [H^+]} \dashrightarrow (8)$$

$$K_{obs} = \frac{K_1 K_2 K_3 [nitrone] [H^+]}{1 + K_1 [H^+]} \dashrightarrow (9)$$

(or)

$$\frac{1}{k_{obs}} = \frac{1}{K_1 K_2 k_3 [nitrone] [H^+]} + \frac{1}{K_2 k_3 [nitrone]}$$

The plot of $1/k_{obs}$ versus $1/[H^+]$ is linear (r = 0.970; sd = 105.5) and from the plot $K_1$ and $K_2 K_3$ are calculated ($K_1$ = 624.54 and $K_2 K_3$ = 0.174). The observed rate constant is consistent with rate law.

### b) *Effect of substituents*

The reaction rate an extension of the present investigation, the kinetics of oxidation of some para-substituted nitrones with PyDC is followed at three different temperatures. The rate data are analysed from the linear free energy relationships [19]. The respective rate constants and the thermodynamic parameters are listed in (Table-4). Isokinetic relationship, the variation in $\Delta S^{\#}$ should be linearly related [20-21] to changes in $\Delta H^{\#}$ by equation (10)

$$\Delta H^{\#} = \Delta H^0 + \beta \Delta S^{\#} \quad \text{-------------}(10)$$

A plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ (Fig-1) gives a straight line with a correlation coefficient r = 0.998. The isokinetic temperature (β)is obtained from the slope is 274K. This temperature is higher than that of experimental temperature, indicating that the reaction is enthalpy controlled. This is further supported by the fact that Ea values are the least for the fast reaction and higher for the slowest reaction. The good correlation implies that the reaction with all the substituted nitrones follow a common mechanism.

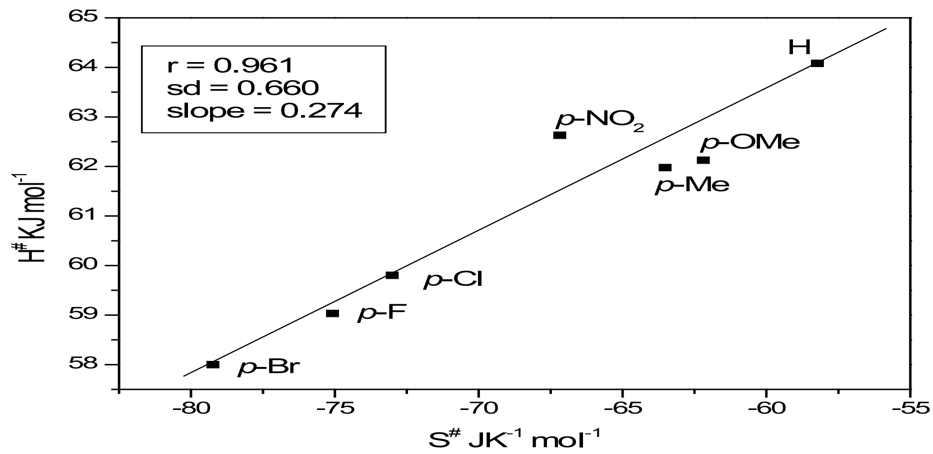


**Fig.1. Plot of $H^{\#}$ versus $S^{\#}$ for oxidation of nitrones by PyDc in aqueous dimethyl sulphoxide medium**

### c) *The Exner's Plot*

However, Exner [22-23] criticised the validity of such a linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ as these quantities depend on each other when measurements at two temperatures are made, the experiment data can be treated by the following equation [24-25].

$$\log k_{2(T1)} = a + b \log k_{2(T2)} \qquad (11)$$

where $T_2 > T_1$

A good correlation (r=0.990) is obtained when $\log k_2$ (25) is plotted against logk (35) shows that the reaction under investigation follows common mechanism.

### d) *Hammett Plot*

The hammet equation applied with the usual substituent constant σ and $k_{obs}$data of Para substituted nitrones exhibits an straight line (Fig-2).The Hammett plot is also linear (r = 0.981, sd =0.023) with ρ = -0.315 at 318K.

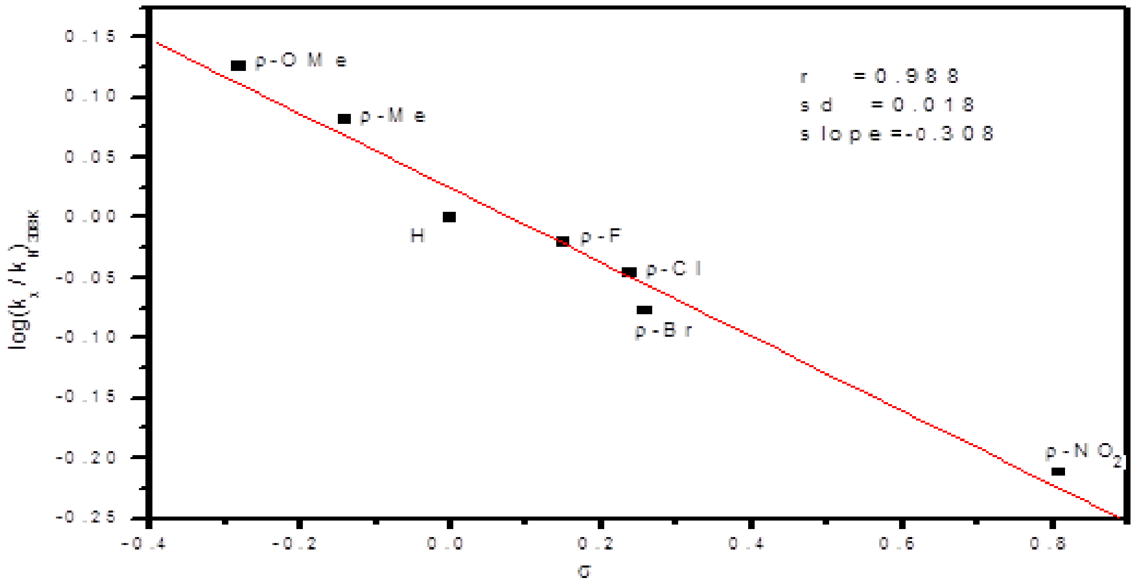


Fig.2. Hammett plot: Plot of log($k_x$/$k_H$) at 308 K versus σ for oxidation of nitrone by pyDC in aqueous-dimethylsulphoxide medium

According to Hammett reaction with positive ρ values are accelerated by electron releasing from phenyl ring, whereas those with negative ρ values are retarded by electron withdrawal from phenyl ring[26]. In this oxidation reactions, the electron withdrawing group increases the rate and the electron donating group decreases the rate. These observations supporting the negative ρ value obtained from the Hammett plot. The order of reactivity of different substituents is as follows.

$$p-\mathrm{OMe} > p-\mathrm{Me} > \mathrm{H} > p-\mathrm{F} > p-\mathrm{Cl} > p-\mathrm{Br} > p-\mathrm{NO_2}$$

The values of reaction constants (ρ) are calculated at different temperatures and summarised in (Table-5). The reaction constant (ρ) has a small negative value as the oxidation involves loss of electrons. The negative value of the reaction constant is acceptable as transition state is involved in positive-charged species.

*Table 5 :* Reaction constants for the oxidation of nitrones by PyDC

| Temp K | ρ | r | sd |
|---|---|---|---|
| 308 | - 0.315 | 0.981 | 0.023 |
| 313 | - 0.331 | 0.995 | 0.011 |
| 318 | - 0.308 | 0.988 | 0.018 |

## IV. CONCLUSION

1. Seven N, α- diphenylnitrones were prepared according to the literature methods. The purity of the nitrones were checked by the TLC method and their physical constants.
2. Pyrazolinium dichromate (PyDC) was prepared and purity of the oxidant was estimated by iodometric method.
3. All the kinetic studies were found by iodometric procedure to starch end point.
4. Kinetics and mechanism of oxidation of N,α-diphenylnitrones by Pyrazolinium dichromate (PyDC) in aqueous DMSO medium was followed under different experimental conditions and temperatures. The reaction followed first order dependence with respect to [PyDC], [Nitrones] and fractional order with respect to [$H^+$].The effect of change in ionic strength and dielectric constant were also studied. The rate of oxidation decreased with increasing [$Mn^{+2}$], which implies the disproportionate of the Cr(IV) by Mn(II). All the above results indicate that a protonated nitrone reacted with chromate ion to form intermediate complex in the slow step. Linear Hammett plot obtained clearly showed that the common mechanism operated under the experimental condition.
5. Isokinetic plots (Exner's and$\Delta H^{\#}$versus $\Delta S^{\#}$) gave satisfactory straight lines with good correlation

coefficient. This proves that all these substituents follow a common mechanism.

## References Références Referencias

1. Sundaram, S. M.; Amutha, M.; and Sockalingam, R.M.*Chem. Environ. Res.,***1996**,5: 229.
2. Mangalam, G.;and Sundaram, S. M.*Oxid. Commun.,***1998**, 21: 68.
3. Corey, E. J.; and Schmidt, G., *Tetrahedron Lett.,***1979**,399.
4. Sutherland, J. K.; Widdowson, D. A. *J. Chem. Soc.***1964**, 3495.
5. Uma, M.; Gopalakrishnan, M.; Jayabharathi, J.; Thanikachalam, V. Kinetics of oxidation of some substituted N,a–diphenylnitrones by bromamine – B in the presence of acid medium. *J. Indian Chem.***1995**, 34(B): 612-616.
6. Uma, M.; Gopalakrishnan, M.; Jayabharathi, J.; Thanikachalam, V. Kinetics of oxidation of some substituted N,a–diphenylnitrones by bromamine – B in the presence of acid medium. *J. Indian Chem. Soc.* **1996**, 73: 329-334.
7. Gopalakrishnan, M.; Jayabharathi, J.; Thanikachalam, V. Separation of electronic and steric effects: oxidation of ortho substituted N,a-diphenylnitrones by pyridiniumfluoro chromate in aqueous DMF medium. *Asian J. Chem.***1999**, 12: 1459-1462.
8. Manivarman, S.; Manikandan, G.; Sekar, M.; Jayabharathi, J.; Thanikachalam, V. Mechanistic investigation of N,α-diphenylnitrones oxidation by N-bromosuccinimide. Non-linear hammett plot. *Oxid.Commun.***2007**, 30: 823-831.
9. Vogel, A. I. "A Text Book of Practical Organic Chemistry" (Longmans, London) 5th Ed. **1989**, 955.
10. Vogel, A. I. "A Text Book of Practical Organic Chemistry" (Longmans, London) 5th Ed. **1989**, 410.
11. Kolthoff, I. M.; Carr, E. M. Volumetric determination of persulfate in presence of organic substances. *Anal. Chem.***1953**, 25: 298-301.
12. Balasubramanian, K., and Prathipa, V., *Indian J. Chem.,***1986***,* 35(B): 326.
13. Chatterjee, A. C.; Mukherjee, S. K. *Z. Phys. Chem.***1957**, 207: 372.
14. Wiberg, K. B.; Mill, T. J. *J. Am. Chem. Soc.***1958**, 80: 3021-3022.
15. Wiberg, K. B. *"Oxidation in Organic Chemistry"* (Academic Press, New York). **1965**, 78.
16. Westheimer, F. H. Chem. Rev., **1949**, 45: 419.
17. Beck, M. T., and Durham, D. A.*J. Inorg. Nucl.Chem.,***1971**,33: 461.
18. (a) Laider, K. J. Chemcial Kinetics. (Tata McGraw Hill. New Delhi), **1982**, p.229;
    (b) Amis, E. S. "Solvent effects on reduction rates and mechanism", Academic press New York. **1967**, 42.
19. Bhandari, A., Sharma, P. K., and Banerji, K. K.*Indian J. Chem.,***2001**, 40(A): 470.
20. Gilberson, N. R., Gallup, G. A., and Jones, M. M.*Trans. Kansas. Acad. Sci.,***1954**, 57: 391.
21. Leffler, J. E. Entropy requirements of the hammett relationship. *J. Chem. Phys.***1955**, 23: 2199.
22. Exner, O. *Collect. Czech. Chem. Commun.***1964**, 29: 1094-1101.
23. Exner, O. Concerning isokinetic relationship. *Nature.***1964**, 201: 488.
24. Palm, V.A.; Vizgest, R. V. *Dokl.Akad,Nauk USSR.***1962**, 142**:** 1091(in Russian).
25. Malawski, M. J. *Rozhiki Chem.***1964**, 38: 1129 (in polish).
26. Hammett, L. P. Physical Organic Chemistry, 1st edn. McGraw-Hill, New York, **1940**.

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