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Separation of Electronic and Steric Effects: Oxidation of *ortho*-substitued N,α-Diphenylnitrones by Pyridinium Fluorochromate in Aqueous DMF Medium

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The kinetics of oxidation of some *ortho*-substituted N,α-diphenylnitrones with pyridinium fluorochromate (PFC) in aqueous DMF medium have been investigated. The rate equation $v = k[\text{nitrone}][\text{oxidant}]$ is found to be valid. Regression analyses of the rate data by using Taft and Charton equation to separate steric effect from electronic effects have been carried out. Results indicate that the steric effect plays a major role while localized and resonance effects play a minor role.

INTRODUCTION

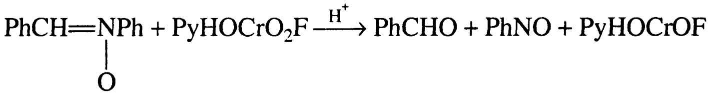
Kinetics and mechanism of oxidation of several organic substrates by pyridinium fluorochromate (PFC)[1–3] are well reported. But there is no systematic kinetic reports on the oxidation of *ortho*-substituted N,α-diphenylnitrons by Cr(VI) complexes. This prompted the authors to undertake this investigation.

EXPERIMENTAL

A mixture of equimolar amounts of the appropriate β-phenylhydroxylamine and benzaldehyde in minimum amount of ethanol was heated on a water bath with occasional shaking for 1 h. The solution was diluted with water till it became turbid. The mixture was allowed to stand at room temperature or in a refrigerator for about 3 h. The nitrone that separated (usually in yields of 80 to 90%) was recrystallised from benzene-petroleum ether (b.p. 40–60°C).

AR aldehydes, sodium perchlorate and perchloric acid were used as such. Commercial grade of DMF was purified by the method described by Vogel[4].

Stoichimetry and product analysis: The reaction mixture containing excess PFC in the presence of perchloric acid were kept for a day. The estimation of unreacted PFC indicated that one mole of PFC was used up for a mole of nitrone



$$\mathrm{PhCH{=}\underset{\substack{|\\ O}}{N}Ph + PyHOCrO_2F \xrightarrow{H^+} PhCHO + PhNO + PyHOCrOF}$$

The reaction mixture was extracted with chloroform and actual kinetic run after about 85% completion of the reaction. The solvent was removed at reduced pressure after drying over anhydrous sodium sulphate. The reaction mixture was monitored by TLC along with authentic samples of N,α-diphenylnitrone, benzaldehyde and nitrobenzene. The reaction mixture gave two spots which became visible by exposure to iodine. They exactly correspond to the R_f value of the authentic samples of benzaldehyde and nitrosobenzene. These products are also analyzed by IR.

The kinetic studies were carried out under pseudo-first order conditions, keeping [nitrone] >> [PFC]. The course of the reaction was followed by estimating the unreacted PFC iodometrically. The reaction was followed at four different temperatures, *viz.*, 30, 35, 40 and 45°C.

The pseudo-first order rate constant, at each kinetic run in PFC, was evaluated from the slopes of the linear plot of log titre versus time. The rate constants k_2 were calculated using the relation

$$k_2 = k_{obs}/[\text{nitrone}]$$

RESULTS AND DISCUSSION

An analysis of the rate data of the *ortho*-substituted N,α-diphenylnitrones shows that these rate are comparatively lower than those of corresponding *meta*-and *para*-isomers. The rate constants and the activation parameters are listed in Table-1. The order of reactivity is

$$H > OCH_3 > CH_3 > F > Cl > Br > NO_2$$

TABLE-1

SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS*

Substituents	$k_2 \times 10^2$ dm^{-3} mol^{-1} s^{-1}				ΔH kJ mol^{-1}	−ΔS J K^{-1} mol^{-1}	r	SD
	Temp. (K)							
	303	308	313	318				
H	10.48	14.30	17.40	30.33	50.25	98.35	0.970	0.12
o-CH_3	10.24	14.00	17.67	25.72	52.68	117.70	0.988	0.05
o-OCH_3	9.68	13.20	17.46	25.35	47.03	109.42	0.996	0.04
o-F	9.23	10.42	17.00	20.14	41.52	119.95	0.960	0.12
o-Cl	8.35	10.01	16.46	19.16	44.14	120.36	0.970	0.11
o-Br	6.93	9.64	15.23	18.87	51.76	96.49	0.990	0.07
o-NO_2	6.75	8.31	12.66	15.85	14.03	122.44	0.985	0.08

Regression analyses have been carried out with Taft's linear free energy, polar energy relationship (equation A) and linear free energy steric relationship (equation B).

$$\log k_{ortho} = \rho_0{}^{*}\sigma_0{}^{*} + h \qquad \text{(A)}$$

$$\log k_{ortho} = \delta E_s + h \qquad \text{(B)}$$

In the above equation σ_0^* (polar) and E_s (steric) are the substitutent constants, ρ_0^* is a reaction constant analogous to ρ, and δ is a steric susceptibility factor. The results of regression analysis with Taft's relationship are expressed by the following equations. At 30°C:

$$\log k_{ortho} = -0.569\ \sigma_0^* \ - = 0.982 \qquad (1)$$

$$(r = 0.852;\ SD = 0.16;\ n = 6)$$

$$\log k_{ortho} = 0.377E_s - 1.221 \tag{2}$$

$$(r = 0.803;\ SD = 0.18;\ n = 6)$$

Gallo[5] suggested that the single parameter treatment is unlikely to be of any general use. Using Taft's linear free energy-polar and steric energy relationship, the data sets are correlated by multiple linear regression analysis.

At 30°C:

$$\log k_{ortho} = \rho_0^* \ \sigma_0^* + \delta E_s + h \tag{C}$$

$$\log k_{ortho} = -0.394\ \sigma_0^* + 0.15E_s - 1.061 \tag{3}$$

(multiple correlation coefficient, $R = 0.788$; $n = 6$; $CL = 95\%$)

Results indicate that the steric contribution seems to be much greater than polar effect of the *ortho*-substitutents.

To understand the composition of localised, delocalised electrical effect and steric effect operating in these reactions, the rate data are analyzed by LD and LDS equation

$$\log k_{ortho} = L\sigma_I + D\sigma_R + h \tag{D}$$

$$\log k_{ortho} = L\sigma_I + D\sigma_R + S\nu + h \tag{E}$$

where σ_I, σ_R and ν are inductive, resonance and steric subtituted constants.

Correlations obtained with LD and LDS equations are justified by F-test significance (> 95% CL in many cases)

$$\log k_{ortho} = -\ 0.333\sigma_I - 927\sigma_R - 1.299 \tag{4}$$

($r = 0.845$; $SD = 0.19$; $n = 6$ unsubstituted excluded —NO_2 group orthogonal)

The L and D terms are significant to 95% CL of t-test

$$\log k_{ortho} = -\ 0.388\sigma_I - 0.67\sigma_R - 1.182 \tag{5}$$

($r - = 0.756$; $SD = 0.2$; $n = 7$ unsubstituted included NO_2 group orthogonal)

The L and D terms are significant to > 95% and 99% CL of T-test

$$\log k_{ortho} = -\ -= 0.30\sigma_I - 0.877\sigma_R - 1.281 \tag{6}$$

($r = 0.756$; $SD = 0.2$; $n = 6$ unsubstituted excluded NO_2 group planar)

The L and D terms are significant to > 95% and 99% CL of t-test

$$\log k_{ortho} = -\ 0.364\sigma_I - 0.685\sigma_R - 1.182 \tag{7}$$

($r = 0.756$; $SD = 0.2$; $n = 6$ unsubstituted included NO_2 group planar)

The L and D terms are significant to > 99% and > 95% CL (t-test) respectively.

From the results of equations 3, 4, 5, 6, 9 and 10 suggest it is clear that when nitro group is in the planar position steric effect is dominant compared to delocalized effect. But when the nitro group is in the orthogonal position delocalised effect is dominant compared to steric effect and the values are listed in Table-2

Mechanism and Rate Law

In this oxidation reaction, at low [H^+], the order with respect to [PFC] is unity.

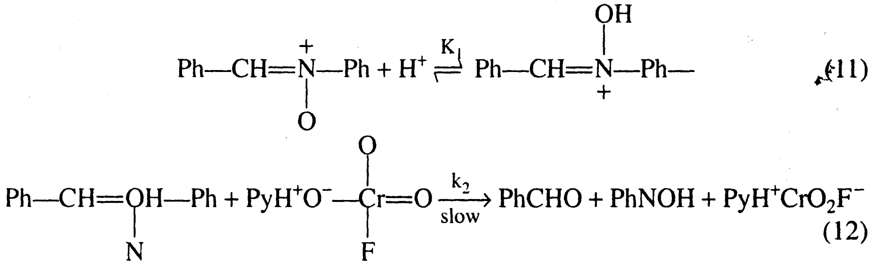
But the order in $[H^+]$ is fractional (0.47). The PFC does not undergo protonation at very low $[H^+]$. The observed salt and solvent effects showed that the reaction is not between ionic species in the slow-step. Owing to the above reasons, the nitrone can protonate before the rate determining step and it can react with PFC in the slow step.

TABLE-2

Equation	P_L	P_D	P_s	n
LD	26.42	73.57	–	6^{o}
	25.48	74.51	–	6^{p}
	36.67	63.32	–	7^{o}
	34.70	65.30	–	7^{o}
LDS	27.65	53.44	18.91	7^{o}
	23.86	76.13	15.80	6^{o}
	19.01	36.17	44.81	7^{p}
	17.88	5.48	76.63	6^{p}

o- Nitro group in orthogonal; *p*- nitro group in planar.

Scheme-1



$$\text{Ph—CH}{=}\underset{\text{O}}{\overset{+}{\text{N}}}\text{—Ph} + \text{H}^+ \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Ph—CH}{=}\underset{+}{\overset{\text{OH}}{\text{N}}}\text{—Ph—} \quad (11)$$

$$\text{Ph—CH}{=}\underset{\text{N}}{\text{OH}}\text{—Ph} + \text{PyH}^+\text{O}^-\text{—}\underset{\text{F}}{\overset{\text{O}}{\text{Cr}}}{=}\text{O} \xrightarrow[\text{slow}]{k_2} \text{PhCHO} + \text{PhNOH} + \text{PyH}^+\text{CrO}_2\text{F}^- \quad (12)$$

$$\text{PhNOH}^+ \xrightarrow[\text{fast}]{k_3} \text{PhNO} + \text{H}^+ \quad (13)$$

The rate law for the suggested mechanism is

$$\frac{-d[\text{PFC}]}{df} = \frac{K_1k_2[\text{PFC}][\text{S}][\text{H}^+]}{1 + K_1[\text{H}^+]} \quad (14)$$

$$k_{obs} = \frac{K_1k_2[\text{S}][\text{H}^+]}{1 + K_1[\text{H}^+]} \quad (15)$$

REFERENCES

1. U. Bhattacharjee and A.K. Bhattacharjee, *Indian J. Chem.*, **19A**, 1187 (1980).
2. R.K. Dhar and R. Varadharajan, *Indian J. Chem.*, **30A**, 936 (1991).
3. S. Agarwal, K. Chowdhury and K.K. Banerji, *J. Org. Chem.*, **56**, 5113 (1991).
4. A.I. Vogel, "A Text Book of Practical Organic Chemistry, Longmanns, London, p. 277 (1978).
5. R. Gallo, *Prog. Phys. Org. Chem.*, **14**, 115 (1982).

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