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Research Article

KINETIC AND MECHANISTIC STUDIES IN THE OXIDATIVE REGENERATION OF CARBONYL COMPOUNDS FROM OXIMES BY PYRIDINIUM DICHROMATE

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ABSTRACT

The oxidative deoximination of several aldo- and keto-oximes by pyridinium dichromate (PDC), in dimethylsulphoxide (DMSO), exhibited a first order dependence on PDC. A Michaelis-Menten type kinetics was observed with respect to oximes. The oxidation of ketoximes is slower than that of aldoximes. Aldoximes rates are correlated with Pavelich-Taft DSP model. Small sigma values (+) are the indication of a nucleophilic hit by an oxygen from chromate the carbon atom. The reaction is subject to alkyl group steric obstruction. One of the aldoximes (acetaldoxime) is subjected to the influence of 19 organic solvent media. Multiparametric equations are used to analyze the influence of organic media. Mechanistic pathways engaging the involvement of an intermediary cyclic structure in r.d.s.

Keywords: Carbonyl compounds, Dichromates, Kinetics, Mechanism, Oxidation, Oximes.

1. INTRODUCTION

Synthetic organic chemists are always interested in renewal of compounds containing carbonyl group compounds in selective and conditions. A large number of oxidation processes are present in the literature [1]. Chromium (VI) derivatives are used as oxidants in chemical processes worldwide. Because of their extreme nature of oxidation and non soluble in most of the media, they cannot be used as a choosy compound. Thus solubility is one of the major difficulties. Avoiding all these problems, various chromium (VI) mild and selective compounds are prepared and available in literature [2-5]. One such compound is also pyridinium dichromate (PDC) reported in literature [6]. A few reports are available in literature regarding oxidation aspects of halochromates and dichromates including PDC [7-10]. Therefore, in the present article, we have reported the oxidation kinetics of several oximes (Aldo & keto) with PDC in DMSO. Mechanistic aspects have also been discussed.

2. EXPERIMENTAL

2.1. Reagents

All the aldo- and keto-oximes were synthesized as per the methods available in literature [11]. Melting points were checked with the literature values. PDC was prepared by the reported method [6]. DMSO and other solvents were either taken as supplied or their purifications were done as per the literature methods [12].

2.2. Analysis of product formation

TLC methods confirmed the formation of oximes as the carbonyl compounds regenerated them. (TLC eluent: CCl_4/Et_2O). Benzaldehyde and acetophenone were taken under oxidation for product Isolation. In a specific experiment, one of the oximes (0.2 mol) and PDC (0.05 mole) were dissolved in 5 deciliter of dimethyl sulphoxide and left for overnight to complete the reaction. Small amount of silica gel was added and mixture was shaken for some time, say fifteen minutes [13]. Product was filtered and washed with solvent (2 % 15 ml). Extra solvent was taken out by rotatory evaporator and the product was purified in a column having silica gel (eluent: CCl_4/Et_2O). The purest variety of carbonyl compound was obtained after removal of all the extra solvent. Yields of benzaldehyde and acetophenone were 1.81 g (85%) and 2.11 g (88%) respectively. The positive starch iodide test confirmed the presence of HNO_2 in reduced reaction mixtures [14]. The oxidation state of chromium was confirmed to be 3.95 ± 0.10 in the reduced reaction mixture.

2.3. Determination of kinetic parameters

All the reactions were done in large excess of reductant over oxidant. In all the reactions, the solvent medium was dimethylsulphoxide only. All the reactions were done at a given constant temperature. All the reactions were monitored in a decreasing order of the concentration of oxidant spectrophometrically at a λ max 352. The pseudo-first-order rate constant, k_{obs}, are calculated from the linear least-squares plots of log [PDC] against time. Reproducibility was checked by reproduction of various kinetic runs with in a range of ±4%. The second order rate constants were evaluated from the relation $k_2 = k_{obs}/[reductant]$.

3. RESULTS AND DISCUSSION

3.1. Stoichiometric determination

The product analysis indicated the following reaction.

$$R_2C=N\text{-}OH + Cr_2O_7^{-2} + 10H^+ \longrightarrow R_2C=O + HNO_2 + 5H_2O + 2Cr^{+3} \quad (1)$$

3.2. Rate Laws

The reactions are of first order with respect to PDC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of PDC. The reaction rate increases with increase in the concentration of the oximes but not linearly (Table 1). The fig.1 depicts a typical kinetic run. A plot of $1/k_{obs}$ against 1/[Oxime] is linear ($r > 0.995$) with an intercept on the rate-ordinate. Thus, fractional order kinetics is seen w.r.t. reductant. The empirical mechanism may be given as below (Equations (2) and (3) and rate law (4).

Table 1: Rate constants for the oxidation of acetaldoxime by PDC at 298 K

10^3 [PDC]	[Oxime]	$10^4 k_{obs}$
mol dm^{-3}	mol dm^{-3}	s^{-1}
1.00	0.10	7.69
1.00	0.20	11.3
1.00	0.40	14.9
1.00	0.60	16.6
1.00	0.80	17.6
1.00	1.00	18.3
1.00	1.50	19.3
1.00	3.00	20.4
2.00	0.20	11.7
4.00	0.20	10.8
6.00	0.20	10.0
8.00	0.20	11.5
1.00	0.40	15.3*

** contained 0.0001 mol dm^{-3} acrylonitrile*

$$\text{Oxime} + \text{PDC} \underset{k_2}{\overset{K}{\leftrightarrows}} [\text{Complex}] \quad (2)$$

$$[\text{Complex}] \longrightarrow \text{Products} \quad (3)$$

$$\text{Rate} = k_2 K [\text{Oxime}] [\text{PDC}]/(1+K [\text{Oxime}]) \quad (4)$$

The dependence of k_{obs} on the concentration of oxime was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots (Fig. 2). The values of K and k2 are used to evaluate the thermodynamic parameters of Oxime-PDC complex and activation parameters of the decomposition of the Oxime-PDC complex, at a temperature 298 K, values are recorded in Tables 2 and 3.

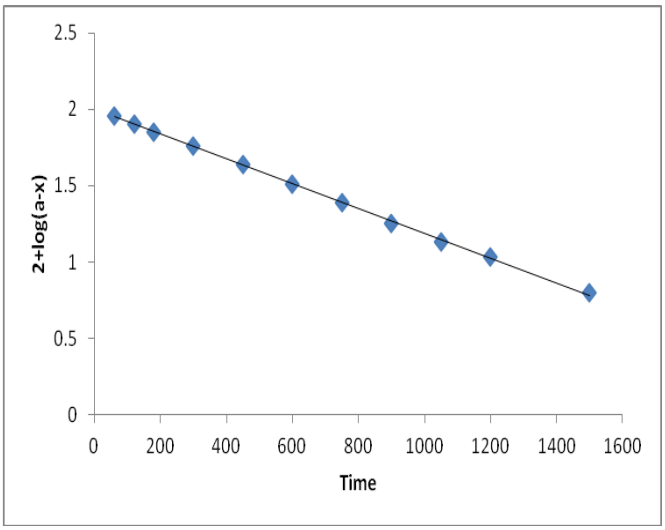


Fig. 1: Oxidation of Acetaldoxime by PDC: A typical Kinetic Run

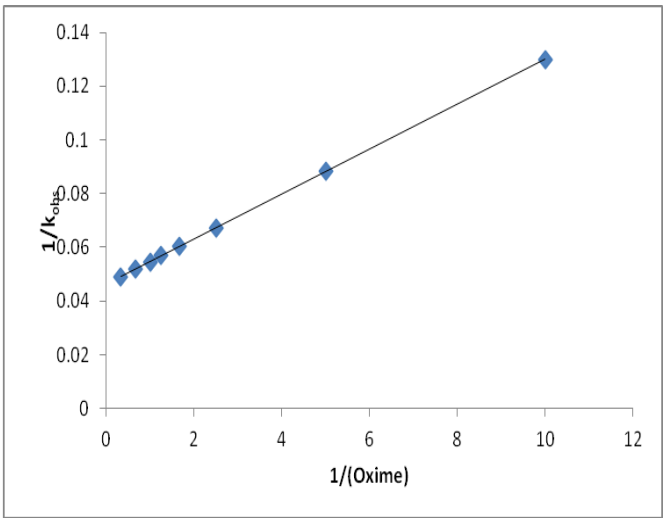


Fig. 2: Oxidation of Acetaldoxime by PDC: A double reciprocal plot

Table 2: Rate constants for the PDC-Oximes (R^1 R^2 C = N - OH) Complexes and their activation parameters

Subst (R)	10^4 k_2 / (dm^3 mol^{-1} s^{-1})				ΔH^*	$-\Delta S^*$	ΔG^*
	288	298	308	318	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
H - H	1330	1500	1640	1660	30.4±0.7	249±1	77.8±0.6
H - Me	18.9	30.6	47.7	69.3	30.6±0.4	186±1	87.0±0.3
H - Et	13.5	21.6	35.1	52.2	32.1±0.4	189±1	88.2±0.3
H - Pr	5.76	10.8	17.1	27.9	37.1±0.9	178±1	90.1±0.7
H - Pr^i	3.78	6.93	12.6	20.7	40.9±0.4	169±1	91.0±0.3
H - $ClCH_2$	70.2	96.3	126	153	17.4±0.7	226±1	84.6±0.6
H - Ph	39.6	58.5	87.3	126	26.9±0.3	198±2	85.7±0.2
Me - Me	1.98	3.15	4.95	7.65	31.8±0.2	206±1	93.0±0.2
Me - Et	1.53	2.34	3.69	5.76	31.2±0.6	210±1	93.7±0.5
Et - Et	1.26	1.98	3.15	4.86	31.8±0.4	209±2	94.1±0.3
Me - Ph	3.42	5.85	9.90	16.2	37.0±0.2	183±1	91.4±0.1

Table 3: Thermodynamic parameters of PDC- Oximes (R^1 R^2 C = N-OH) Complexes and their formation constants

Substituent (R)	K / (dm^3 mol^{-1})				$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
	288	298	308	318	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
H - H	6.39	5.61	4.77	3.99	14.5±0.5	26±2	6.72±0.4
H - Me	5.94	5.15	4.35	3.51	15.7±0.8	32±2	6.51±0.6
H - Et	6.31	5.53	4.68	3.90	14.7±0.6	27±2	6.68±0.5
H - Pr	5.85	5.06	4.23	3.45	15.7±0.8	32±3	6.47±0.7
H - Pr^i	5.58	4.80	3.96	3.18	16.7±0.7	36±2	6.32±0.6
H - $ClCH_2$	5.76	4.93	4.14	3.35	14.8±0.6	33±2	6.41±0.5
H - Ph	6.03	5.25	4.40	3.63	15.4±0.6	30±2	6.55±0.5
Me - Me	6.13	5.35	4.50	3.73	15.1±0.6	29±2	6.60±0.5
Me - Et	5.90	5.07	4.29	3.49	15.7±0.6	32±2	6.48±0.5
Et - Et	5.49	4.70	3.89	3.06	17.2±0.9	37±3	6.27±0.7
Me - Ph	5.67	4.88	4.05	3.26	16.5±0.7	35±2	6.36±0.6

3.3. Influence of Solvent media

The acetaldoxime is oxidized and studied in 19 various organic solvent media. Due to solubility problem of reactants, we have limited choice of solvent media. Solvents so taken have no specific reactions with solvent media. Almost all the solvents showed similar kinetics. The data for K and k_2 are given in the table 4.

We do not observe any noteworthy isokinetic relating behaviour in activation entropy and enthalpy of the oxidation of oximes (r^2 = 0.4431). Sometimes calculated values of activation enthalpy and entropy go away because of some errors combine with them. Exner [15] has suggested an alternative method of testing the validity of the isokinetic relationship. An Exner's plot between log k_2 at 288 and 318 K was linear (r^2 = 0.9978; slope = 0.7434 ± 0.0171) (Figure-3). The isokinetic temperature evaluated from this plot is 456±17 K. this correlation is suggesting that all the reactants are oxidizing at a same mechanism behavious.

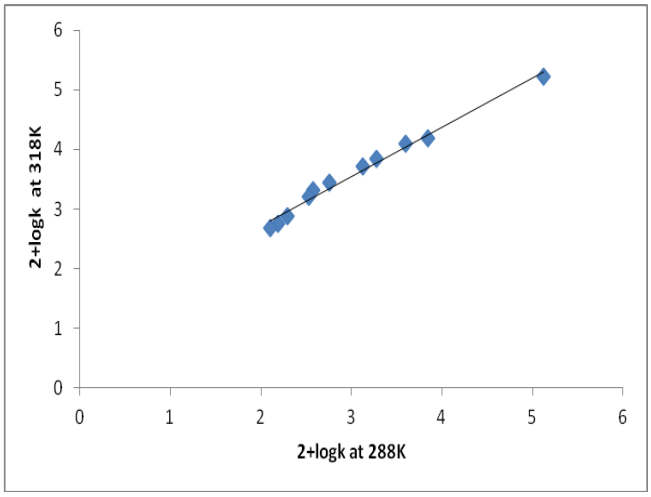


Fig. 3: Oxidation of oximes with similar isokinetic relationship by PDC

Table 4: Influence of solvent media on the oxidation of acetaloxime by PDC at 288 K

Solvents	K (dm^{-3} mol^{-1})	10^5 k_{obs} (s^{-1})	Solvents	K (dm^{-3} mol^{-1})	k_{obs} (s^{-1})
Chloroform	4.88	47.9	Toluene	5.49	12.3
1,2-Dichloroethane	5.58	56.2	Acetophenone	5.55	79.4
Dichloromethane	5.39	63.1	THF	5.87	27.5
DMSO	5.94	189	t-Butylalcohol	4.98	20.0
Acetone	4.99	51.3	1,4-Dioxane	5.71	24.0
DMF	5.49	97.7	1,2-Dimethoxyethane	4.92	14.4
Butanone	5.81	33.9	CS_2	5.85	7.08
Nitrobenzene	5.50	77.6	Acetic Acid	4.72	12.0
Benzene	5.80	15.8	Ethyl Acetate	5.68	18.2
Cyclohexane	5.63	1.66			

3.4. Solvent Effect

The rate constants, k_2, of acetaldoxime in 18 solvents (CS_2 is not considered, as the whole data range is not available) are correlated in terms of the LSER (Eq.5) of Kamlet et al. [16].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (5)$$

In this equation, π^* represents the solvent polarity, β is basicities of hydrogen bone acceptor, α is acidity for donor of hydrogen bond. A_0 is known to be the intercept data. We clarify the 12 solvent media the value is zero for α against 18 taken into studies. The data so obtained of correlation analyses in terms of Eq. (5), a biparametric equation involving π^* and β, and separately with π^* and β are given below [Eqs. (6)-(9)].

$$\log k_2 = -3.73 + 1.76\ (\pm 0.18)\ \pi^* + 0.19\ (\pm 0.15)\ \beta + 0.04\ (\pm 0.15)\ \alpha \quad (6)$$

$R^2 = 0.8886$; sd = 0.17; n = 18; $\psi = 0.36$

$$\log k_2 = -3.74 + 1.77\ (\pm 0.17)\ \pi^* + 0.18\ (\pm 0.14)\ \beta \quad (7)$$

$R^2 = 0.8879$; sd = 0.16; n = 18; $\psi = 0.35$

$$\log k_2 = -3.71 + 1.82\ (\pm 0.17)\ \pi^* \quad (8)$$

$r^2 = 0.8759$; sd = 0.17; n = 18; $\psi = 0.36$

$$\log k_2 = -2.71 + 0.50\ (\pm 0.38)\ \beta \quad (9)$$

$r^2 = 0.0969$; sd = 0.46; n = 18; $\psi = 0.98$

n denotes the data point and ψ is Exner's statistical parameter [17].

Kamlet's [16] triparametric equation explains *ca.* 89% data on the effect of solvent. But as per the Exner's expression [17], this correlation does not fall under the category of satisfaction. (cf. Eq. 6). It has been observed that solvent polarity plays an important role as it explains 87% of data on its own, whereas β & α are playing play negligible part in it.

Due to non-effective role of Kamlet model, the same data are fitted in another model of solvent effect known as Swain's model [18] of cation- and anion-solvating concept of the solvents also [Eq. (10)].

$$\log k_2 = aA + bB + C \quad (10)$$

In the above equation, A is denoted the anion-solvating power of the solvent and B represents the cation-solvating power. Here C is denoted as the term of intercept. Solvent polarity is denoted by (A + B). The rate data so obtained are analysed as per equation 10.

$$\log k_2 = 0.83\ (\pm 0.04)\ A + 1.78\ (\pm 0.03)\ B - 3. \quad (11)$$

$R^2 = 0.9949$; sd = 0.04; n = 19; $\psi = 0.07$

$$\log k_2 = 0.57\ (\pm 0.59)\ A - 2.71 \quad (12)$$

$r^2 = 0.0531$; sd = 0.47; n = 19; $\psi = 0.99$

$$\log k_2 = 1.72\ (\pm 0.15)\ B - 3.67 \quad (13)$$

$r^2 = 0.8858$; sd = 0.17; n = 19; $\psi = 0.35$

$$\log k_2 = 1.46 \pm 0.12\ (A + B) - 3.91 \quad (14)$$

$r^2 = 0.8903$; sd = 0.16; n = 19; $\psi = 0.34$

Excellent correlation was found, when the rates of oxidation of acetaldoxime in various solvents are fitted with Swain's model [cf. Eq.(11)], where both A and B played their roles at par. Whereas, cation and anion solvating powers showed only 05% and 88% data explaining the solvent effect. A good correlation was also observed with solvent polarity. Factually, solvent polarity explains 89% of the data on solvent effect, therefore we tried to correlate the rate of oxidation with relative permittivity. However, a plot of $\log k_2$ and inverse of the relative permittivity is not found to be noteworthy ($r^2 = 0.5535$; sd = 0.33; $\psi = 0.69$). The solvent effect indicated that activated complex so formed is more polar as compared to the reactants. It has been observed that the rate of the reaction is dependent on the polarity of the solvents.

3.5. Correlation Analysis of Reactivity

No report is available in the literature about the mechanistic aspects of C = N and halochromates. However, the reaction of alkenes with Cr (VI) has already been studied at length. [19]. It has been

observed that olefinic bonds are not attacked by nucleophilic reagents, therefore it is suggested at first stage organometallic compound is formed during alkene-chromate reaction [19], and then this compound converts to Cr (IV) di-ester in r.d.s. it has also been observed that C = N bonds, are easily attacked by nucleophile. The data recorded in the table 2 indicated that the rates of aldo-oximes are much higher as compared to keto-oximes. As the central carbon is changing from trigonal to tetragonal, the rates of keto-oximes are slower, as the crowding around it increases. Keto-oximes are more crowded as compared to aldo-oximes. This observation is supported by the correlation analysis of the reactivity of the aldoximes also. Aliphatic oxime rates are not going to give a good correlation in terms of Tafts's σ^* & E_S values [Eqs. (15) and (16)]. These rates are than correlated with Pavelich-Taft's [20] DSP equation (17).

$$\log k_2 = 1.15\pm0.65\ \sigma^* - 2.58 \quad (15)$$

$r^2 = 0.4345$, sd = 0.71, n = 6, ψ=0.82, Temp.=298 K

$$\log k_2 = 1.25\pm0.27\ E_S - 2.38 \quad (16)$$

$r^2 = 0.8464$, sd =0.37, n=6, ψ = 0.43, Temp. =298 K

$$\log k_2 = \rho^*\sigma^* + \delta E_S + \log k_0 \quad (17)$$

The rates exhibited excellent correlations in terms of the Pavelich-Taft equation (Table 5); the reaction constants are being positive.

3.6. Mechanistic pathways

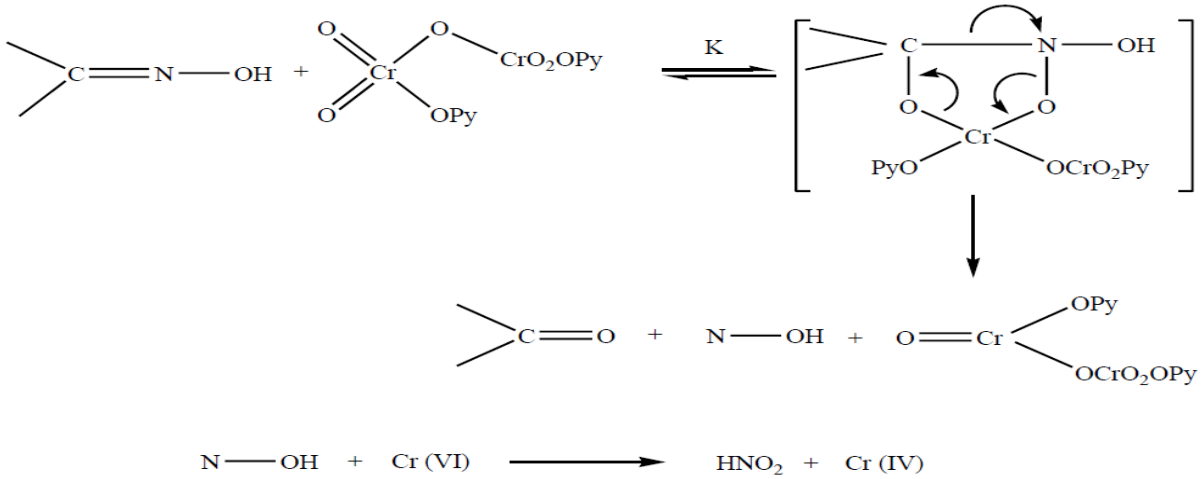
The presence of low positive values for polar reaction constant indicating the formation of a cyclic transition state N - O bond is formed later the bond formation between chromate-oxygen and the carbon. This is supported by a nucleophilic attack of chromate-oxygen on the carbon. The positive steric reaction constant indicates the steric hindrance by the substituents. On the basis of these observations, Scheme 1 is proposed as its reaction mechanism. The mechanistic pathway is also supported by the values of activation parameters also. The low values of enthalpy of activation indicate that the bond-cleavage and bond-formation are almost synchronous. The large negative entropies of activation support the formation of a rigid cyclic activated complex from two acyclic structures.

In the faster oxidation of benzaldoxime cyclic activated complex is stabilized due to resonance. Due to bulky phenyl & methyl group hindrance the oxidation of benzphenoxime is much slower. It has been reported that Hydroxynitrene (N-OH) as a highly reactive intermediate [21].

Table 5: Reaction constants for the oxidative deoximination of aliphatic aldoximes by PDC[a]

Temp./ K	ρ^*	δ	r^2	Sd	ψ
288	0.81±0.01	1.17±0.01	0.9999	0.008	0.01
298	0.72±0.01	1.07±0.01	0.9998	0.010	0.02
308	0.63±0.01	0.99±0.01	0.9989	0.009	0.04
318	0.54±0.01	0.90±0.01	0.9999	0.005	0.01

[a] *Number of compounds is 6*



Scheme - 1

4. CONCLUSION

Oxidation of oximes by PDC proceeds via a cyclic intermediate in the r.d.s. The reaction is sterically hindered by the alkyl group. Oxidation of ketoximes is slower than aldoxime.

5. ACKNOWLEDGEMENTS

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Conflict of interest

None declared

Source of funding

None declared

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