



# KINETICS AND MECHANISM OF THE OXIDATIVE REGENERATION OF CARBONYL COMPOUNDS FROM OXIMES BY TETRAETHYLAMMONIUM CHLOROCHROMATE

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## ABSTRACT

The oxidative deoximation of several aldo- and keto-oximes by tetraethylammonium chlorochromate (TEACC), in dimethylsulphoxide, exhibited a first order dependence on both; the oxime and TEACC. The oxidation of ketoximes is slower than that of aldoximes. The rates of oxidation of aldoximes correlated well in terms of Pavelich-Taft dual substituent-parameter equation. The low positive value of polar reaction constant indicated a nucleophilic attack by a chromate-oxygen on the carbon. The reaction is subject to steric hindrance by the alkyl groups. The reaction of acetaldoxime has been studied in nineteen different organic solvents. The solvent effect has been analysed by multiparametric equations. A mechanism involving the formation of a cyclic intermediate, in the rate-determining step is suggested.

**Key words:** Carbonyl compounds, Halochromates, Kinetics, Mechanism, Oxidation, Oximes.

## INTRODUCTION

Regeneration of carbonyl compounds from its derivatives under mild conditions is an important process in synthetic organic chemistry. Several oxidative methods are available for deoximation<sup>1</sup>. Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry<sup>2-6</sup>. Tetraethylammonium chlorochromate (TEACC) is also one such reagent<sup>7</sup>. There seems to be no report, on the kinetic and mechanistic aspects of oxidation of oximes by TEACC. We have been interested in the kinetics of reactions of complexed Cr (VI) species and have already published a few reports on the kinetics and

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mechanism of the oxidation by pyridinium and quinolinium halochromates<sup>8-10</sup>. Therefore in continuation of our earlier work, we report here the kinetics of the oxidative deoxygenation of several aldo- and keto-oximes by TEACC in several organic solvents but mainly in dimethylsulphoxide (DMSO). Mechanistic aspects have also been discussed.

## EXPERIMENTAL

### Materials

Oximes were prepared by the reported standard methods<sup>11</sup> and their m. p. were checked with the literature values. TEACC was also prepared by the reported method<sup>7</sup>. Solvents were purified by the usual procedure<sup>12</sup>.

### Product analysis

The oxidation of the oximes results in the regeneration of corresponding carbonyl compounds, as confirmed by TLC (eluent: CCl<sub>4</sub>/Et<sub>2</sub>O). Isolation of the product was attempted in the oxidation of oximes of benzaldehyde and acetophenone. In a typical experiment, the oxime (0.2 mol) and TEACC (0.02 mol) were dissolved in 50 mL of DMSO and allowed to stand for *ca.* 10 h for the completion of the reaction. Silica gel (5 g) was then added to the reaction mixture and the mixture was stirred for 15 min<sup>13</sup>. It was then filtered and the solid residue was washed with the solvent (2 % 15 mL). The solvent was removed on a rotary evaporator and the residue was purified on a silica-gel column (eluent: CCl<sub>4</sub>/Et<sub>2</sub>O). Evaporation of the solvent afforded the pure carbonyl compound. Yields of benzaldehyde and acetophenone were 1.79 g (84%) and 2.13 g (89%), respectively. The presence of HNO<sub>2</sub> in completely reduced reaction mixtures was confirmed by a positive starch-iodide test<sup>14</sup>. The oxidation state of chromium in a completely reduced reaction mixture, as determined by an iodometric method, is  $3.90 \pm 0.10$ .

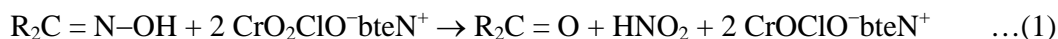
### Kinetics measurements

The reactions were studied under pseudo-first-order conditions by keeping a large excess ( $\times 10$  or greater) of the oxime over TEACC. The solvent was DMSO, unless mentioned otherwise. The reactions were studied at constant temperature ( $\pm 0.1$  K). The reactions were followed by monitoring the decrease in the concentration of TEACC at 370 nm spectrophotometrically. The pseudo-first-order rate constant,  $k_{\text{obs}}$ , was evaluated from the linear least-squares plots of  $\log [\text{TEACC}]$  versus time. Duplicate kinetic runs showed the rate constants to be reproducible within  $\pm 4\%$ . We have used coefficient of determination ( $R^2$  or  $r^2$ ), standard deviation (sd) and Exner's<sup>15</sup> parameter,  $\psi$ , as the measures of goodness of fit.

## RESULTS AND DISCUSSION

### Stoichiometry

The analysis of products indicated the following overall reaction.



TEACC undergoes a two-electron change, which is in accord to our earlier observations with structurally similar halochromates.

### Rate laws

The reaction is first order with respect to TEACC. The individual kinetic runs yielded linear ( $r^2 > 0.995$ ) plots between  $\log [\text{TEACC}]$  and time. Further, the values of  $k_{\text{obs}}$  do not depend on the initial concentration of TEACC. The reaction exhibited a linear dependence on the concentration of the oximes (Table 1). Fig. 1 depicts a typical kinetic run.

**Table 1: Rate constants for the oxidation of acetaldxime by TEACC at 298 K**

$\frac{10^3 [\text{TEACC}]}{(\text{mol dm}^{-3})}$	$\frac{[\text{Oxime}]}{(\text{mol dm}^{-3})}$	$\frac{10^4 k_{\text{obs}}}{(\text{s}^{-1})}$
1.0	0.1	6.80
1.0	0.2	13.5
1.0	0.4	27.1
1.0	0.6	40.5
1.0	0.8	54.5
1.0	1.0	68.4
0.5	0.4	28.8
2.0	0.4	26.1
3.0	0.4	27.0
4.0	0.4	28.2
5.0	0.4	27.3

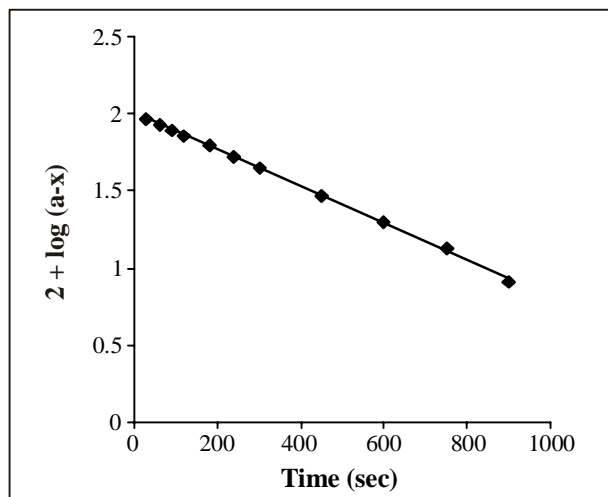


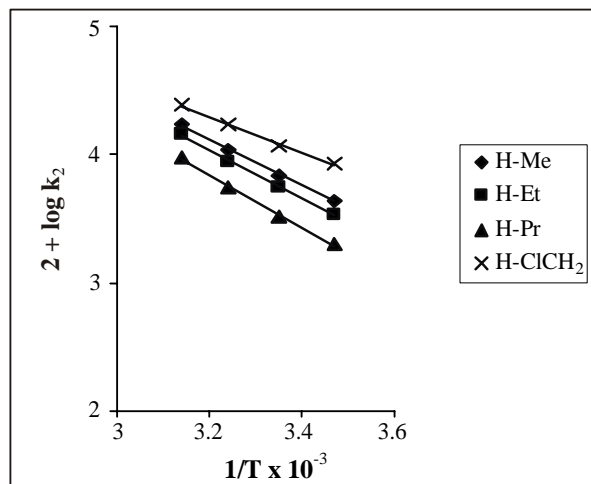
Fig. 1: Oxidation of acetaldoxime by TEACC: A typical kinetic run

### Effect of temperature

The rate constants were determined at different temperatures and the activation parameters were calculated (Table 2). The  $\log k_2$  at different temperature is linearly related to the inverse of the absolute temperature in all cases (Fig. 2). The Arrhenius equation is, therefore, valid for these oxidations.

Table 2: Rate constants and activation parameters for the oxidation of oximes ( $R^1 R^2 C = N - OH$ ) by TEACC

Substituent	$10^4 k_2$ ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )				$\Delta H^*$	$\Delta S^*$	$\Delta H^*$
	288 K	298 K	308 K	318 K	( $\text{kJ mol}^{-1}$ )	( $\text{J mol}^{-1} \text{K}^{-1}$ )	( $\text{kJ mol}^{-1}$ )
H H	738	918	1150	1440	$14.5 \pm 0.3$	$-217 \pm 1$	$78.9 \pm 0.2$
H Me	44.1	68.4	108	171	$31.9 \pm 0.6$	$-180 \pm 2$	$85.3 \pm 0.5$
H Et	34.2	55.8	89.1	144	$33.9 \pm 0.4$	$-175 \pm 1$	$85.8 \pm 0.3$
H Pr	19.8	33.3	55.8	93.6	$36.9 \pm 0.5$	$-169 \pm 2$	$87.1 \pm 0.4$
H $\text{Pr}^I$	15.3	25.2	43.2	75.6	$39.4 \pm 0.6$	$-163 \pm 2$	$87.8 \pm 0.5$
H $\text{ClCH}_2$	83.7	117	171	243	$24.6 \pm 0.6$	$-199 \pm 2$	$84.0 \pm 0.5$
H Ph	89.1	135	216	324	$30.5 \pm 0.6$	$-179 \pm 2$	$83.6 \pm 0.5$
Me Me	4.41	6.84	10.8	16.2	$30.7 \pm 0.3$	$-203 \pm 1$	$91.0 \pm 0.3$
Me Et	3.51	5.40	8.46	12.6	$30.1 \pm 0.3$	$-207 \pm 1$	$91.6 \pm 0.3$
Et Et	2.79	4.32	6.75	10.8	$31.8 \pm 0.7$	$-203 \pm 2$	$92.2 \pm 0.6$
Me Ph	7.83	12.6	18.9	28.8	$30.3 \pm 0.3$	$-199 \pm 1$	$89.6 \pm 0.2$



**Fig. 2: Oxidation of oximes by TEACC: Effect of temperature**

### Effect of solvents

The oxidation of acetaldoxime was studied in nineteen different solvents. The choice of solvents was limited due to the solubility of the reactants and the reaction of TEACC with primary and secondary alcohols. There was no reaction with chosen solvents. The kinetics were similar in all the solvents. The values of  $k_2$  are recorded in Table 3.

**Table 3: Effect of solvent on the oxidation of acetaldoxime by TEACC at 318 K**

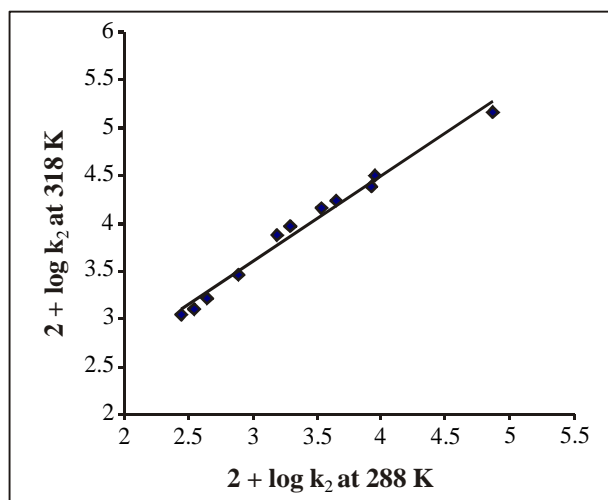
Solvent	$\frac{10^4 k_2}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	Solvent	$\frac{10^4 k_2}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
Chloroform	63.1	Toluene	9.77
1,2-Dichloroethane	51.3	Acetophenone	53.7
Dichloromethane	57.5	Tetrahydrofuran	18.2
DMSO	171	t-BuOH	27.5
Acetone	41.7	Dioxane	22.4
Dimethylformamide	77.6	1,2-Dimethoxyethane	10.5
Butanone	33.9	Acetic acid	30.2
Nitrobenzene	66.1	Ethyl acetate	14.8
Benzene	12.0	Carbon disulfide	5.25
Cyclohexane	1.12		

**Table 4: Reaction constants for the oxidative deoxygenation of aliphatic aldoximes by TEACC<sup>a</sup>**

Temp./K	$\rho^*$	$\delta$	$R^2$	sd	$\psi$
278	$0.45 \pm 0.01$	$0.81 \pm 0.02$	0.9998	0.006	0.02
288	$0.39 \pm 0.02$	$0.75 \pm 0.03$	0.9999	0.004	0.01
298	$0.35 \pm 0.01$	$0.70 \pm 0.02$	0.9989	0.003	0.04
298	$0.29 \pm 0.01$	$0.63 \pm 0.01$	0.9999	0.001	0.01

<sup>a</sup>Number of compounds is 6

The linear correlation ( $r^2 = 0.9946$ ) between the values of the activation enthalpies and entropies of the reaction indicated the operation of a significant compensation effect in this reaction<sup>16</sup>. The reaction exhibited an excellent isokinetic effect (temperature  $450 \pm 17$ ) also, as determined by Exner's method<sup>17</sup>. An Exner's plot between  $\log k_2$  at 288 K and at 318 K is linear ( $r^2 = 0.9972$ , slope =  $0.7541 \pm 0.0198$ ) (Fig. 3). The value of isokinetic temperature is  $466 \pm 23$  K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all reactions so correlated follow a similar mechanism<sup>15</sup>.

**Fig. 3 Exner's isokinetic relationship in the oxidation of oximes by TEACC**

### Solvent effect

The rate constants,  $k_2$ , of the oxidation of acetaldoxime in eighteen solvents (CS<sub>2</sub>

was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (Eq. 2) of Kamlet et al.<sup>18</sup>

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad \dots(2)$$

In this equation,  $\pi^*$  represents the solvent polarity,  $\beta$  the hydrogen bond acceptor basicities and  $\alpha$  is the hydrogen bond donor acidity.  $A_0$  is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for  $\alpha$ . The results of correlation analyses in terms of Eq. (2), a biparametric equation involving  $\pi^*$  and  $\beta$  and separately with  $\pi^*$  and  $\beta$  are given below [Eqs. (3) - (6)].

$$\log k_2 = -3.89 + 1.88 (\pm 0.20) \pi^* + 0.13 (\pm 0.17) \beta + 0.42 (\pm 0.16) \alpha \quad \dots(3)$$

$$R^2 = 0.8794; \text{sd} = 0.18; n = 18; \psi = 0.38$$

$$\log k_2 = -3.78 + 1.73 (\pm 0.23) \pi^* + 0.27 (\pm 0.19) \beta \quad \dots(4)$$

$$R^2 = 0.8183; \text{sd} = 0.22; n = 18; \psi = 0.45$$

$$\log k_2 = -3.73 + 1.80 (\pm 0.23) \pi^* \quad \dots(5)$$

$$r^2 = 0.7930; \text{sd} = 0.23; n = 18; \psi = 0.47$$

$$\log k_2 = -2.78 + 0.58 (\pm 0.39) \beta \quad \dots(6)$$

$$r^2 = 0.1223; \text{sd} = 0.47; n = 18; \psi = 0.96$$

Kamlet's<sup>18</sup> triparametric equation explains *ca.* 88% of the effect of solvent on the oxidation. However, by Exner's criterion<sup>15</sup> the correlation is not even satisfactory (cf. Eq. 3). The major contribution is of solvent polarity. It alone accounted for *ca.* 79% of the data. Both  $\beta$  and  $\alpha$  play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's equation<sup>19</sup> of cation- and anion-solvating concept of the solvents also [Eq. (7)].

$$\log k_2 = aA + bB + C \quad \dots(7)$$

Here  $A$  represents the anion-solvating power of the solvent and  $B$  the cation-solvating power.  $C$  is the intercept term.  $(A + B)$  is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of Eq. (7), separately with  $A$  and  $B$  and with  $(A + B)$ .

$$\log k_2 = 1.48 (\pm 0.04) A + 1.69 (\pm 0.03) B - 3.90 \quad \dots(8)$$

$$R^2 = 0.9963; \text{sd} = 0.03; n = 19; \psi = 0.06$$

$$\log k_2 = 1.24 (\pm 0.56) A - 2.93 \quad \dots(9)$$

$$r^2 = 0.2271; \text{ sd} = 0.45; n = 19; \psi = 0.90$$

$$\log k_2 = 1.57 (\pm 0.26) B - 3.62 \quad \dots(10)$$

$$r^2 = 0.6768; \text{ sd} = 0.29; n = 19; \psi = 0.58$$

$$\log k_2 = 1.62 \pm 0.04 (A + B) - 3.91 \quad \dots(11)$$

$$r^2 = 0.9920; \text{ sd} = 0.06; n = 19; \psi = 0.09$$

The rates of oxidation of acetaldehyde in different solvents showed an excellent correlation in Swain's equation [cf. Eq. (8)] with both the anion- and cation-solvating powers playing almost equal role. However, individually A and B are able to account for only 23% and 68% of the data only. The solvent polarity, represented by (A + B), also exhibited an excellent correlation. In view of the fact that solvent polarity is able to account for *ca.* 99% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of  $\log k_2$  against the inverse of the relative permittivity is not very significant ( $r^2 = 0.4784$ ;  $\text{sd} = 0.37$ ;  $\psi = 0.74$ ).

### Correlation analysis of reactivity

We could not find any report about the mechanism of the reaction between a C=N bond and a halochromate derivative. However, the reaction of alkenes with chromium (VI) has been well studied<sup>20</sup>. Since, olefinic bonds are not usually subject to a nucleophilic attack, it has been suggested that in the alkene-chromate reaction, an organometallic derivative is formed initially<sup>20</sup>. The organometallic derivative then changes to a chromium (IV) diester in the rate-determining step. However, carbon-nitrogen double bonds, being dipolar in nature, can be easily attacked by a nucleophile. The data in table 2 showed that the rate of oxidation of ketoximes is much less as compared to that of the aldoximes. The reason for the slower reaction of ketoximes must be steric. As the central carbon changes from a trigonal to a tetragonal state, the crowding around it increases. This increase in the steric crowding will be more in the case of ketoximes as compared to that in aldoximes. This observation is supported by the correlation analysis of the reactivity of the aldoximes also. The rate of oxidation of the aliphatic oximes did not yield significant correlation separately with Taft's  $\sigma^*$  and  $E_S$  values [Eqs. (12) and (13)]. The rates were, therefore, correlated with Pavelich-Taft's<sup>21</sup> dual substituent-parameter Eq. (14).

$$\log k_2 = 0.69 \pm 0.46 \sigma^* - 2.21 \quad \dots(12)$$

$$r^2 = 0.3643, \text{ sd} = 0.50, n = 6, \psi = 0.87, \text{ Temp.} = 298 \text{ K}$$



$$\log k_2 = 0.85 \pm 0.15 E_S - 2.09 \quad \dots(13)$$

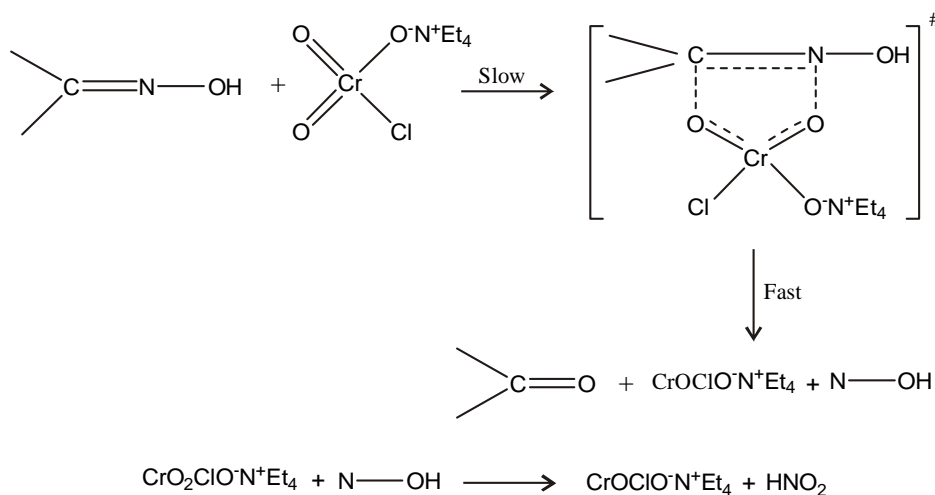
$$r^2 = 0.8944, \text{sd} = 0.20, n = 6, \psi = 0.36, \text{Temp.} = 298 \text{ K}$$

$$\log k_2 = \rho^* \sigma^* + \delta E_S + \log k_0 \quad \dots(14)$$

The rates exhibited excellent correlations in terms of the Pavelich-Taft equation (Table 4); the reaction constants are being positive.

## MECHANISM

The low positive polar reaction constant points to an almost cyclic transition state in which the formation of the bond between chromate-oxygen and the carbon is somewhat ahead of the formation of N – O bond. This supports a nucleophilic attack by a chromate-oxygen on the carbon. The positive steric reaction constant points to a steric hindrance by the substituents. Therefore, the following mechanism (**Scheme 1**) is proposed for the reaction. The mechanism is 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 molecules.



**Scheme 1**

The faster oxidation of benzaldoxime may be attributed to the resonance stabilization of the cyclic activated complex. The oxidation of benzphenoxime is much slower. This may well be due to steric hindrance by the bulky phenyl and methyl groups. Hydroxynitrene (N-OH) has been reported as a very reactive intermediate<sup>22</sup>.

## ACKNOWLEDGEMENTS

Thanks are due to the UGC (New Delhi) for financial support Prof. K. K. Banerji, Dean, Sciences, NLU, Mandore, Jodhpur, for valuable suggestions.

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*Revised : 03.11.2011*

*Accepted : 07.11.2011*