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KINETICS AND MECHANISM OF THE OXIDATIVE REGENERATION OF CARBONYL COMPOUNDS FROM OXIMES BY PYRIDINIUM FLUOROCHROMATE

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Abstract

Oxidative deoximination of aldoximes and ketoximes by pyridinium fluorochromate proceeds by nucleophilic attack of the chromate oxygen on the oxime carbon to give a cyclic intermediate in the rate-determining step.

Keywords: Deoximination, chromium (VI), kinetics, mechanism

INTRODUCTION

Regeneration of carbonyl compounds from their derivatives under mild conditions is an important process in synthetic organic chemistry. Several oxidative methods are available for deoximination [1]. Pyridinium fluorochromate (PFC) has been reported as a useful and mild oxidizing reagent [2]. There seems to be no report about the kinetics and mechanism of oxidative deoximination by PFC. We report here the kinetics of the oxidative deoximination of several aldoximes and ketoximes by PFC in dimethyl sufoxide (DMSO). Mechanistic aspects are discussed.

EXPERIMENTAL

Oximes were prepared by the reported standard methods. PFC also was prepared by the reported method [2].

The oxidation of the oximes results in the regeneration of the corresponding carbonyl compounds, as confirmed by TLC (eluent: CCl_4/Et_2O). 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 PFC (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 [3]. It was then filtered and the solid residue was washed with the solvent (2 x 15 mL). The solvent was removed on a rotary evaporator and the residue was purified on a silica-gel column (eluent: CCl_4/Et_2O). Evaporation of the solvent afforded the pure carbonyl compound. Yields of benzaldehyde and acetophenone were 0.93 g (88%) and 1.11 g (84%) respectively. The oxidation state of chromium in a completely reduced reaction mixture, as determined by a iodometric method, is 4.02 ± 0.07. The reactions were studied under pseudo-first-order conditions by keeping a large excess (10-fold or greater) of the oxime over PFC. The solvent was DMSO. The reactions were followed by monitoring the decrease in the concentration of PFC at 356 nm spectrophotometrically. The pseudo-first-order rate constant, k_{obs}, was evaluated from the linear least-squares plots of log [PFC] *versus* time. The second order rate constant, k_2, was obtained from the relation: $k_2 = k_{obs}/[oxime]$.

Table 1

Rate constants for the oxidative deoximination of acetaldoxime by PFC at 288 K

10^3[PFC ($mol\ dm^{-3}$)	[oxime] ($mol\ dm^{-3}$)	$10^4\ k_{obs}$ (s^{-1})
1.0	0.1	9.73
1.0	0.2	19.9
1.0	0.3	29.0
1.0	0.5	48.5
1.0	0.8	78.1
1.0	1.0	97.0
1.0	1.4	134
0.5	0.8	77.4
2.0	0.8	78.0
3.0	0.8	79.2
4.0	0.8	78.5
1.0	0.5	48.9[*]

[*] 0.001 $mol\ dm^{-3}$ acrylonitrile added

RESULTS AND DISCUSSION

The analysis of products indicated the following overall reaction.

$$R_2\text{-}C = N\text{-}OH + 2\,CrO_2FO^-PyH^+ \rightarrow R_2\text{-}C = O + HNO_2 + 2\,CrOFO^-PyH^+$$
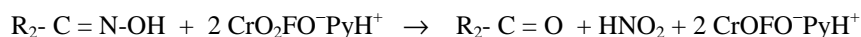
The reaction is first order with respect to both the oxime and PFC (Table 1). The rate constants were determined at different temperatures and the activation parameters were calculated (Table 2). The oxidation of acetaldoxime, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, there is no effect of the addition of acrylonitrile on the rate. Therefore, a one-electron oxidation, giving rise to free radicals is unlikely.

Table 2

Rate constants and activation parameters of the oxidative deoxyimination of oximes ($R^1 R^2 C = NOH$) by PFC

Substituent		$10^4 k_2 / dm^3\,mol^{-1}\,s^{-1}$			ΔH^*	ΔS^*	ΔG^*
R^1	R^2	278 K	288 K	298 K	$kJ\,mol^{-1}$	$J\,mol^{-1}\,K^{-1}$	$kJ\,mol^{-1}$
H	H	2480	3170	4060	14.5±0.2	- 205±1	75.3±0.2
H	Me	62.5	97.0	149	27.4±0.2	- 189±1	83.5±0.2
H	Et	47.2	75.1	122	31.4±0.6	- 183±1	85.7±0.5
H	Pr	22.5	37.5	58.6	30.4±0.5	- 186±2	85.8±0.4
H	Pr^i	15.3	28.0	53.0	40.2±1.0	- 154±4	86.0±0.9
H	$ClCH_2$	135	186	253	19.1±0.4	- 212±2	82.1±0.3
H	Ph	341	462	618	18.0±0.4	- 208±1	79.9±0.3
Me	Me	16.6	27.1	44.2	31.8±0.6	- 184±2	86.5±0.5
Me	Et	12.5	22.5	38.7	36.4±0.4	- 170±2	86.8±0.4
Et	Et	8.65	14.9	24.3	33.1±0.6	- 185±2	87.9±0.5
Me	Ph	5.34	9.48	17.3	37.9±1.0	- 171±3	88.8±0.8

We could not find any report about the mechanism of the reaction between a C=N bond and PFC. However, the reaction of alkenes with chromium (VI) has been well-studied [4]. Since olefinic bonds are usually not susceptible to a nucleophilic attack, it has been suggested that in the alkene-chromate reaction, an organometallic derivative is formed initially. The organometallic derivative then changes to a chromate (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 correlation analysis of the reactivity of aliphatic aldoximes also. The rate of oxidation of the aliphatic aldehydes did not yield significant correlation separately with Tafts's σ^* and E_S values. The rates were, therefore, correlated with the Pavelich-Taft's [5] dual substituent-parameter equation.

$$\log k_2 = \rho^* \sigma^* + \delta E_S + \log k_0$$

The rates exhibited excellent correlations in terms of the Pavelich-Taft equation (Table 3), the reaction constants being positive.

Table 3

Reaction constants for the oxidative deoximination of aliphatic aldoximes by PFC[a]
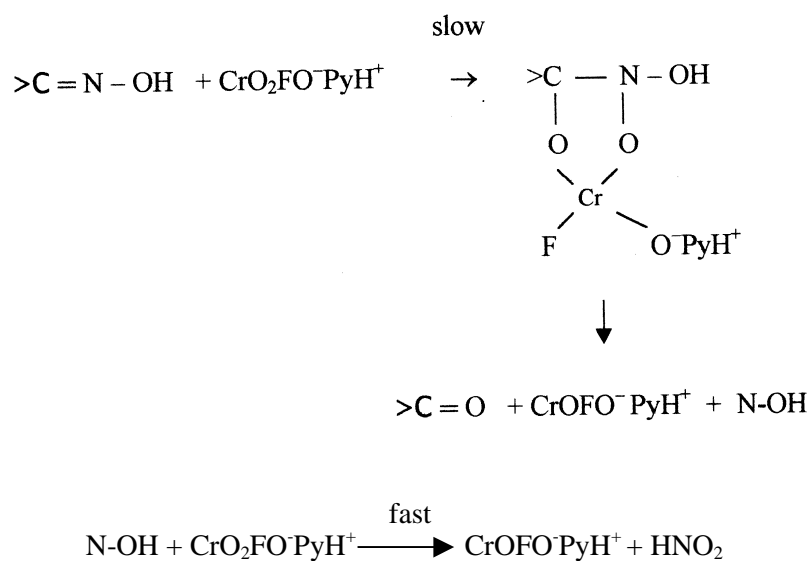
Temp./K	ρ^*	δ	R^2	sd	ψ
278	0.56±0.01	1.07±0.01	0.9998	0.01	0.01
288	0.49±0.02	1.01±0.02	0.9996	0.02	0.03
298	0.41±0.04	0.96±0.03	0.9978	0.04	0.05

[a]No. of compounds = 6

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 the N – O bond. This supports a nucleophilic attack by a chromate-oxygen on the carbon. The positive steric reaction constant points to 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 too. The low values of activation enthalpy indicate that 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.

Hydroxynitrene (N-OH) has been recently reported as a very reactive intermediate [6].

Scheme 1

slow

$$>C = N - OH \;\; + CrO_2FO^-PyH^+ \;\;\; \rightarrow$$

$$>C \;—\; N - OH$$

$$\begin{array}{cc} | & | \\ O & O \end{array}$$

$$\diagdown \diagup$$

$$Cr$$

$$\diagup \diagdown$$

$$F \qquad O^-PyH^+$$

$$\downarrow$$

$$>C = O \;\; + CrOFO^- PyH^+ \; + \; N\text{-}OH$$

fast

$$N\text{-}OH + CrO_2FO^-PyH^+ \xrightarrow{\hspace{1cm}} CrOFO^-PyH^+ + HNO_2$$

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