J. Chem. Research (S),
2001, 127–128
J. Chem. Research (M),
2001, 0428–0439

Kinetics and mechanism of the oxidative regeneration of carbonyl compounds from oximes by cetyltrimethylammonium permanganate

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The oxidative deoximination of several aldo- and keto-oximes by cetyltrimethylammonium permanganate (CTAP), in dichloromethane, proceeding through the formation of a cyclic intermediate, in the rate-determining step, has been proposed.

Keywords: carbonyl compounds, oximes, certyltrimethylammoniun permargante

Cetyltrimethylammonium permanganate (CTAP) has been reported as a useful reagent for the regeneration of carbonyl compounds from their oximes and 2,4-dinitrophenylhydrazones.[2] There seems to be no report about the kinetics and mechanism of oxidative deoximation by a permanganate derivative. We report here the kinetics of the oxidative deoximation of several aldo- and keto-oximes by CTAP in dichloromethane.

Oximes were prepared by the reported standard methods. CTAP also was prepared by the reported method.[3] Successive scans of the oxidation of acetaldoxime by CTAP, in the UV-VIS region, were obtained, on a HP Diode-Array rapid scanning spectrophotometer (Model 8452A) with a scanning speed of 600 nm/s.

The oxidation of the oximes results in the regeneration of corresponding carbonyl compounds. The oxidation state of manganese in a completely reduced reaction mixture, as determined by an iodometric method, is 3.87±0.11. The overall reaction may be represented as follows:

$$\begin{aligned}&3\,R_2\text{- C = N-OH} + 4\,MnO_4^- \rightarrow\\&\quad 3\,R_2\text{- C = O} + 3\,HNO_2 + 2\,MnO_2 + 2\,MnO_3^{2-}\end{aligned}\qquad(1)$$

The reactions were studied under pseudo-first-order conditions by keeping a large excess (× 10 or greater) of the oxime over CATP. The solvent was dichloromethane. The reactions were followed by monitoring the decrease in the concentration of CTAP at 529 nm spectrophotometrically. The pseudo-first-order rate constant, k_{obs}, was evaluated from the linear least-squares plots of log [CTAP] *versus* time.

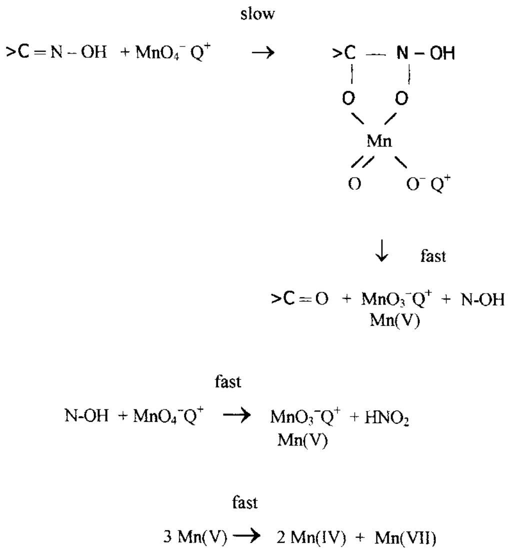
The reaction is first order with respect to both the oxime and CTAP. The rate constants were determined at different temperatures and the activation parameters were calculated.

When the progress of the reaction is monitored by UV-VIS spectroscopy, a series of curves were obtained. Thus the reaction is simple from the spectrophotometric point of view. An excellent isosbestic point is obtained at 475 nm, when the reaction is monitored by absorption spectroscopy. This suggests that the reaction is analytically simple *i.e.* there are no complicating side reactions.

The reaction of alkenes with permanganate ion has been well studied.[8] Since, olefinic bonds are not usually subject to a nucleophilic attack, it has been suggested that in the alkene-permanganate reaction, an organometallic derivative,[9] containing a C – Mn bond, is formed initially. The organometallic derivative then changes to a manganese (V) diester in the rate-determining step. However, carbon–nitrogen double bonds, being dipolar in nature, can be easily attacked by a nucleophile. 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 tetrahedral 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 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 Pavelich-Taft's[10] dual substituent-parameter equation (4).

$$\log k_2 = \rho^*\,\sigma^* + \delta\,E_S + \log k_0 \qquad (4)$$

The rates exhibited excellent correlations in terms of the Pavelich–Taft equation (Table 3); the reaction constants are being positive. The low positive polar reaction constant points to a cyclic transition state in which the formation of the bond between permanganate-oxygen and the carbon is somewhat ahead of the formation of N – O bond. This supports a nucleophilic attack by a permanganate-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.



Scheme 1

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Table 3 Reaction constants for the oxidative deoximination of aliphatic aldoximes by CTAPa

Temp./K	ρ^*	δ	R^2	sd	ψ
278	0.60±0.02	1.16±0.01	0.9996	0.02	0.02
288	0.51±0.03	1.12±0.02	0.9992	0.03	0.02
298	0.46±0.02	1.10±0.01	0.9998	0.01	0.01

[a] No. of compounds = 6.

Hydroxynitrene (N–OH) has been recently reported as a very reactive intermediate.[18]

Thanks are due to University Grants Commission (India) for the financial support and to the referee for valuable suggestions.

Techniques used: Absorption spectroscopy, Chromatography, Correlation Analysis

Table 1. Rate constants for the oxidative deoximination of acetaldoxime by CTAP at 288 K

Table 2. Rate constants and activation parameters of the oxidative deoximination of oximes (R^1 R^2 C = NOH) by CTAP

Figure 1. Successive scans for the oxidation of acetaldoxime (0.003 mol dm^{-3}) by CTAP (0.0004 mol dm^{-3}) in dichloromethane at 303 K (isosbestic point at 475 nm)

References: 18 Figure: 1

Received 30 April 2000; accepted 30 November 2000
Paper 00/302

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