

Kinetics & Mechanism of Epoxidation of Substituted N-Methyl-4-styrylpyridinium Iodides by Alkaline Hydrogen Peroxide

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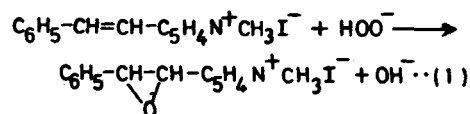
The kinetics of epoxidation of various N-methyl-4-styrylpyridinium iodides by alkaline hydrogen peroxide have been studied in 50% ethanol-50% water (v/v) mixture spectrophotometrically. The reaction is first order in [substrate] and fractional order each in $[H_2O_2]$ and $[OH^-]$. Structure-reactivity study with various 3'- and 4'-substituted-N-methyl-4-styrylpyridinium iodides shows that the reaction rate is accelerated by electron-withdrawing substituents and retarded by electron-donating substituents. A Hammett ρ -value of +0.909 is obtained. A suitable mechanism involving the attack of HOO^- ion on the β -carbon atom to form an intermediate complex which decomposes to the epoxide in a slow step is proposed.

A number of investigations have been reported in literature¹⁻¹³ on the epoxidation of α,β -unsaturated compounds by hydrogen peroxide. It has been reported that the reactions follow overall second order kinetics, first order each in [substrate] and $[H_2O_2]$ and proceed by the slow initial attack of hydroperoxide anion on the β -carbon atom followed by the expulsion of hydroxide ion with concomitant formation of epoxide ring. The literature survey reveals that the epoxidation of substituted N-methyl-4-styrylpyridinium iodides has not been reported. The present paper deals with the detailed kinetic studies on the epoxidation of 3'- and 4'-substituted N-methyl-4-styrylpyridinium iodides by alkaline hydrogen peroxide in ethanol-water mixture.

Materials and Methods

Substituted N-methyl-4-styrylpyridinium iodides (I) were prepared according to literature method and their purities checked by PMR spectra, physical constants and elemental analyses. Ethanol was purified by the usual method. The hydrogen peroxide solution was standardised using standard potassium permanganate solution. The solution of required strength was prepared in 1:1 ethanol-water (v/v) mixture and used in kinetic runs. Sodium hydroxide used was of AR (BDH) grade.

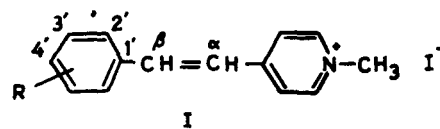
The kinetic measurements were carried out at 25°, 30°, 35° and 45°C under pseudo-first order conditions ($[H_2O_2] \gg [Substrate]$) in 1:1 ethanol-water (v/v)



mixture by monitoring the disappearance of UV absorption maxima at 344, 326, 338, 348, 348, 346, 348, 349, 359 and 412 nm for 4'-nitro-, 3'-nitro-, 3'-chloro-, 4'-bromo-, 4'-fluoro-, H, 3'-methyl-, 4'-methyl- and 4'-methoxy-styryl N-methylpyridinium iodides respectively.

The UV absorption spectra of the N-methyl-4-styrylpyridinium iodides exhibited one intense characteristic absorption in the near visible region^{14,15}. In the present study the UV absorption spectrum of the compound after the completion of the reaction did not show any absorption in the near visible region, indicating the oxidation of the double bond.

The stoichiometry of the reaction was studied by estimating the unreacted hydrogen peroxide in the reaction mixture (where $[H_2O_2] \gg [Substrate]$) after the completion of the reaction. The stoichiometry was found to be 1:1 and the reaction can be represented by Eq. (1).



Results and Discussion

The kinetic results can be summarised as follows:

(i) The reaction is first order in [substrate] as shown by the linearity of the plots of log (absorbance) versus time (correlation coefficient, $r > 0.995$) and also by the constant value of the pseudo-first order rate constants at different initial [substrate] and constant $[H_2O_2]$.

(ii) The plot of log k_1 versus log $[H_2O_2]$ is linear ($r = 0.994$) with a slope of 0.673, indicating that the order

in $[H_2O_2]$ is fractional. Also a plot of $1/k_1$ versus $1/[H_2O_2]$ is linear ($r=0.997$) with a definite intercept on the ordinate indicating Michaelis-Menten type of kinetics.

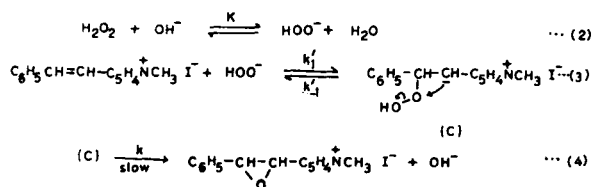
(iii) The rate constant increases with increase in $[OH^-]$. A plot of $\log k_1$ versus $\log [OH^-]$ is linear ($r=0.982$) with a slope of 0.581 indicating fractional order in $[OH^-]$.

(iv) Rate of the reaction increases with increase in the ethanol content in the reaction medium. For example, under the conditions $[substrate]=4 \times 10^{-5}$, $[H_2O_2]=[NaOH]=5 \times 10^{-3}$ mol dm^{-3} and 30° , $10^4 k_1$ increased from 1.98 to 50.50 s^{-1} when % ethanol (v/v) was increased from 30 to 90 in the solvent medium leading to the inference that the reaction is sensitive to the dielectric constant of the medium.

Mechanism and rate law

On the basis of the foregoing kinetic results, the mechanism (Scheme 1) envisaging the attack of hydroperoxide anion on the β -carbon atom of the substrate to form complex (C) which decomposes to the epoxide in a slow step, may be proposed for the oxidation of N-methyl-4-styrylpyridinium iodides.

In the epoxidation of mesityl oxide and of ethylideneacetone by hydrogen peroxide, Bunton and Minkoff³ postulated that the epoxidation proceeded by the slow initial attack of hydroperoxide anion on the β -carbon atom followed in a concerted manner by ring closure and elimination of OH^- anion from the adduct. Epoxidation of α,β -unsaturated ketones^{1,2} and α,β - and β,γ -unsaturated sulphones¹³, were also reported to be second order and proceed by a similar mechanism. But the present results show that the reaction is fractional order in $[H_2O_2]$, and follows Michaelis-Menten type kinetics. This clearly points that the rate-determining step of the reaction is the decomposition of the complex (C) into epoxide.



Scheme 1

Applying steady state approximation,

$$\frac{d[C]}{dt} = k_1'[S][HOO^-] - k'_{-1}[C] - k[C] = 0 \quad \dots (5)$$

i.e. $k_1'\{[S]_0 - [C]\}[HOO^-] - k'_{-1}[C] - k[C] = 0$ (6) where $[S]$ and $[S]_0$ represent the free and total concentration of the substrate (S) respectively. Hence,

$$[C] = \frac{k_1'[S]_0[HOO^-]}{k_1'[HOO^-] + k'_{-1} + k} \quad \dots (7)$$

Since $k \ll \{k_1'[HOO^-] + k'_{-1}\}$, Eq. (7) becomes Eq. (8)

$$[C] = \frac{k_1'[S]_0[HOO^-]}{k_1'[HOO^-] + k'_{-1}} \quad \dots (8)$$

The rate law for the reaction can be written as

$$-\frac{d[NMSPI]}{dt} = k[C] \quad \dots (9)$$

Substituting the value for $[C]$,

$$-\frac{d[NMSPI]}{dt} = \frac{kk_1'[S]_0[HOO^-]}{k_1'[HOO^-] + k'_{-1}} \quad \dots (10)$$

Since $[H_2O_2] \gg [NMSPI]$ in the present reaction, Eq. (10) becomes,

$$k_1 = \frac{kk_1'[HOO^-]}{k'[HOO^-] + k'_{-1}} \quad \dots (11)$$

(where k_1 is the observed pseudo-first order rate constant). Equation (11) can be rearranged to Eq. (12)

$$\frac{1}{k_1} = 1/k + \frac{1}{K'Kk[H_2O_2][OH^-]} \quad \dots (12)$$

The proposed mechanism and rate law are consistent with the observed results.

The pseudo-first order rate constants for unsubstituted N-methyl-4-styrylpyridinium iodide are $2.66 \times 10^{-4} s^{-1}$, $3.73 \times 10^{-4} s^{-1}$, $5.12 \times 10^{-4} s^{-1}$ and $10.8 \times 10^{-4} s^{-1}$ at 25° , 30° , 35° and $45^\circ C$ respectively. The first order decomposition rate constants (k), evaluated from the plot of $1/k_1$ versus $1/[H_2O_2]$, are $0.80 \times 10^{-3} s^{-1}$, $1.00 \times 10^{-3} s^{-1}$, $1.43 \times 10^{-3} s^{-1}$ and $2.00 \times 10^{-3} s^{-1}$ at 25° , 30° , 35° and $45^\circ C$ respectively. The activation parameters ΔH^\ddagger and ΔS^\ddagger have been evaluated from the Eyring's plot ($\log k/T$ versus $1/T$) ($r=0.987$) and the values are found to be 35.4 kJ mol^{-1} and -292 JK $^{-1}$ mol^{-1} respectively.

Substituent effect

The rates of oxidation of several 3'- and 4'-substituted N-methyl-4-styrylpyridinium iodides have been studied at constant $[NaOH]$ and $[H_2O_2]$ and the rate data are given in Table 1. The kinetic runs have also been carried out at different $[H_2O_2]$ at $30^\circ C$ and the first order decomposition constants have been evaluated for each substrate (Table 1). The results clearly indicate that electron-attracting substituents increase the rate while electron-donating substituents

Table 1—Effect of Structural Variation on the Rate of Oxidation

{[H₂O₂] ≫ [Substrate]; Solvent: 1:1 ethanol-water (v/v) mixture; [H₂O₂] = 5.00 × 10⁻³ mol dm⁻³; [NaOH] = 5.00 × 10⁻³ mol dm⁻³}

Substituent	$k_1 \times 10^4 \text{ s}^{-1}$				$a_k \times 10^4 \text{ s}^{-1}$ at 30°C
	25°C	30°C	35°C	45°C	
4'-NO ₂	13.9	19.2	28.1	45.0	55.6
3'-NO ₂	13.2	18.4	26.6	45.0	50.6
3'-Cl	4.87	6.07	10.3	19.5	19.1
4'-Br	4.74	5.89	8.08	17.8	17.4
4'-Cl	3.96	5.86	9.17	16.5	15.4
4'-F	3.18	4.39	6.31	13.4	11.1
H	2.66	3.73	5.12	10.8	10.0
3'-Me	2.41	3.31	4.86	9.40	8.69
4'-Me	2.23	2.79	4.10	8.58	6.66
4'-OMe	1.98	2.77	4.15	8.03	6.45

(a) evaluated from the plot of $1/k_1$ versus $1/[H_2O_2]$ for each substrate.

retard it. Hammett correlation has been carried out and the positive ρ -value of 0.909 ($r=0.994$) suggests that the reaction centre is electron-rich in the transition state and is thus consistent with the proposed mechanism. A comparable ρ -value of +0.920 has been reported in the oxidation of both α,β -unsaturated ketones¹² and α,β -unsaturated sulphones¹³ by alkaline hydrogen peroxide. The logarithms of observed rate constants (k_1) at 30°C also correlate

satisfactorily with the Hammett σ constants ($r=0.983$; $\rho = +0.850$).

An excellent correlation ($r=0.997$) obtained in the isokinetic relationship¹⁶⁻¹⁸ indicates that the epoxidation of all the 3'- and 4'-substituted N-methyl-4-styrylpyridinium iodides by H₂O₂ follow an identical mechanism.

Acknowledgement

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