

Structure-reactivity correlations in the reaction of substituted N-methyl-2-styrylpyridinium iodides with alkaline hydrogen peroxide

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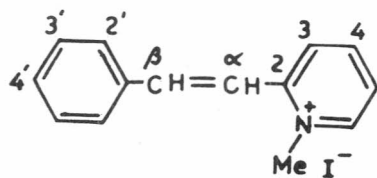
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The kinetics of reaction between N-methyl-2-styrylpyridinium iodides and alkaline hydrogen peroxide have been studied spectrophotometrically in 1:1 (v/v) water-methanol mixture. The reaction is first order in [substrate], $[H_2O_2]$ and $[OH^-]$. Structure-reactivity study with various 2'- and 4'-substituted N-methyl-2-styrylpyridinium iodides shows that the reaction is accelerated by electron-withdrawing substituents and retarded by electron-releasing substituents. A Hammett ρ -value of $+0.916 \pm 0.064$ ($r=0.988$; $s=0.063$) is obtained. A suitable mechanism involving the attack of hydroperoxide ion on the β -carbon atom of the substrate to form epoxide in a slow step followed by cleavage of epoxide is proposed. Analysis of *ortho*-effects using multiparameter extensions of the Hammett equation in the reaction of 2'-substituted-N-methyl-2-styrylpyridinium iodides with alkaline hydrogen peroxide shows that both localised and delocalised effects are important and the steric effect is insignificant.

In continuation of our earlier work¹ on the kinetics of reaction of substituted N-methyl-4-styrylpyridinium iodides by alkaline hydrogen peroxide, we report herein the results of studies on the kinetics of reaction of substituted N-methyl-2-styrylpyridinium iodides with alkaline hydrogen peroxide. In this study are also reported the mechanism of reaction and the effect of 4'- and 2'-substituents on reaction rate. The effect of 2'-substituents on the rate of oxidation has been quantitatively evaluated by applying multiparameter extensions of the Hammett equation.

Materials and Methods

Substituted N-methyl-2-styrylpyridinium iodides (see I) were prepared according to literature methods^{2,3} and their purities checked by their m.ps/b.ps, elemental analyses and ¹H NMR spectra. Methanol was purified according to standard procedure⁴. Sodium hydroxide used was of AR (BDH) grade. Hydrogen peroxide (E Merck) was standardised using standard potassium permanganate solution.



Kinetic measurements

The solvent used was methanol-water (1:1, v/v) mixture. The rate measurements were carried out at 25°, 30°, 35° and 40°C under pseudo-first order conditions ($[H_2O_2] \gg [substrate]$) by monitoring the disappearance of UV absorption maxima of the substrates, viz. 365, 351, 336, 340, 342, 333, 337, 361, 342, 331, 333 and 313 nm for 4'-methoxy-, 4'-methyl-, unsubstituted, 4'-chloro-, 4'-bromo-, 4'-cyano-, 4'-nitro-, 2'-methoxy-, 2'-methyl-, 2'-chloro-, 2'-fluoro- and 2'-nitrostyryl-N-methylpyridinium iodides respectively. The kinetics were followed upto 60% or more and pseudo-first order rate constants were calculated from the slopes of the plots of $\log[\text{absorbance}]$ versus time using a least squares programme. The precision of rate constants is given in terms of 95% confidence limit.

Product analysis

A mixture of N-methyl-2-styrylpyridinium iodide and alkaline hydrogen peroxide under kinetic conditions was kept overnight. It was found that the substrate was cleaved by the oxidant to form a mixture consisting of benzaldehyde (yield 60%) and benzoic acid. However, we were not able to isolate and identify the other part of the cleavage product, i.e. the other carbonyl compound. Estimation of the residual hydrogen peroxide showed that 1 mole of the substrate consumed 2.8 mole of hydrogen peroxide. The cleavage of the substrate to form two carbonyl fragments accounts for

Table 1—Effect of varying [substrate], [H₂O₂] and [OH⁻] on the rate of the reaction at 30°C

(Solvent: 1:1 methanol-water (v/v) mixture)

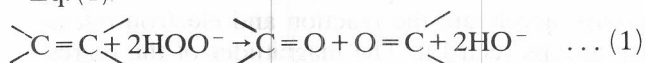
[Substrate] × 10 ⁵ (mol dm ⁻³)	[H ₂ O ₂] × 10 ³ (mol dm ⁻³)	[OH ⁻] × 10 ³ (mol dm ⁻³)	k ₁ × 10 ⁴ (s ⁻¹)
4.0	6.0	6.0	5.02 ± 0.05
5.0	6.0	6.0	4.86 ± 0.04
6.0	6.0	6.0	4.98 ± 0.02
8.0	6.0	6.0	4.82 ± 0.02
10.0	6.0	6.0	4.79 ± 0.02
8.0	3.0	6.0	2.51 ± 0.02
8.0	4.0	6.0	3.26 ± 0.02
8.0	5.0	6.0	4.25 ± 0.12
8.0	7.0	6.0	5.76 ± 0.05
8.0	9.0	6.0	7.29 ± 0.04
8.0	15.0	6.0	13.87 ± 0.25
8.0	30.0	6.0	23.20 ± 0.07
8.0	6.0	3.0	2.30 ± 0.02
8.0	6.0	4.0	3.07 ± 0.02
8.0	6.0	5.0	3.86 ± 0.03
8.0	6.0	7.0	5.57 ± 0.02
8.0	6.0	9.0	7.11 ± 0.02
8.0	6.0	14.0	11.15 ± 0.10
8.0	6.0	30.0	22.54 ± 0.58

Table 2—Effect of varying solvent composition on the rate of the reaction at 30°C

[substrate] = 8 × 10⁻⁵ mol dm⁻³;
[H₂O₂] = [OH⁻] = 6 × 10⁻³ mol dm⁻³

Methanol % (v/v)	k ₁ × 10 ⁴ (s ⁻¹)	Methanol (v/v)	k ₁ × 10 ⁴ (s ⁻¹)
20	2.51 ± 0.02	60	6.30 ± 0.08
30	3.86 ± 0.03	70	10.03 ± 0.11
40	4.39 ± 0.03	80	11.10 ± 0.04
50	4.82 ± 0.02	90	12.29 ± 0.06

2 mole of hydrogen peroxide in accordance with Eq. (1).



Larger concentration of oxidant led to the possibility of further oxidation of carbonyl compounds, the primary oxidation products.

Results and Discussion

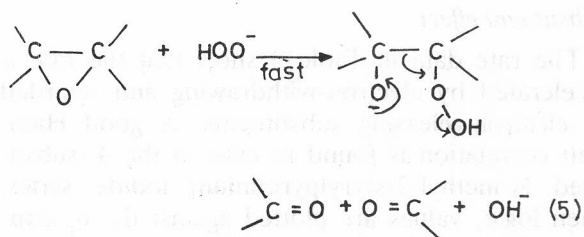
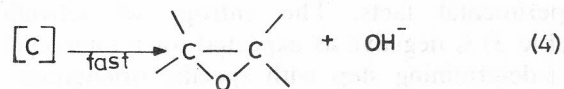
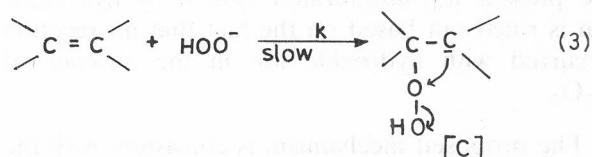
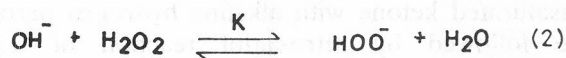
The rates of reaction with change in [substrate], [H₂O₂] and [OH⁻] are given in Table 1. The reaction is first order in [substrate] as shown by the linearity of the plots of log(absorbance) versus time (r > 0.995) and also by the constant value of pseudo-first order rate constants at different initial [substrate] at fixed [H₂O₂] and [OH⁻]. The pseu-

do-first order rate constants increase with the increase in [H₂O₂]. The plot of log k₁ versus log[H₂O₂] is linear (r = 0.998) with a slope of 0.994 indicating that the order in [H₂O₂] is unity. The rate constant increases with increase in [OH⁻] (Table 1). A plot of log k₁ versus log[OH⁻] is linear (r = 0.999) with a slope of 0.996 indicating first order dependence in [OH⁻]. The rate of the reaction increases with increase in methanol content of the reaction medium, i.e. the rate increases with decrease in dielectric constant of the system (Table 2). This indicates interaction between an ion and a dipole in the rate-limiting step. Addition of NaClO₄ to the reaction mixture, has negligible effect on the reaction rate. Under the conditions, [substrate] = 8 × 10⁻⁵ mol dm⁻³; [H₂O₂] = [OH⁻] = 6 × 10⁻³ mol dm⁻³; solvent = 50% methanol-50% water and at 30°C, the rate constants are 4.02, 4.38 and 4.80 × 10⁻⁴ s⁻¹ at [NaClO₄] = 0.001, 0.006 and 0.01 mol dm⁻³ respectively. This shows that there is no need to maintain the ionic strength in this reaction series. Addition of acrylonitrile fails to inhibit the rate indicating that the reaction proceeds by an ionic mechanism.

Mechanism

On the basis of the foregoing kinetic results a mechanism shown in Scheme 1 can be postulated for the reaction of N-methyl-2-styrylpyridinium iodides with alkaline hydrogen peroxide.

The mechanism envisages the attack of HOO⁻ ion on the β-carbon atom of the substrate in a



Scheme 1

Table 3—Pseudo-first order rate constants and activation parameters for the oxidation of 2'- and 4'-substituted N-methyl-2-styrylpyridinium iodides by alkaline hydrogen peroxide in 50% methanol-50% water (v/v) mixture

X	$k_1 \times 10^4 (s^{-1})$				ΔH^\ddagger (kJ mol ⁻¹) (at 30°)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹) (at 30°)	k_0/k_p (at 30°)
	25°	30°	35°	40°			
4'-OMe	2.11 ± 0.02	3.70 ± 0.16	5.44 ± 0.08	7.02 ± 0.10	59.6 ± 2.1	114.3 ± 7.3	—
4'-Me	2.57 ± 0.02	4.33 ± 0.03	6.26 ± 0.09	8.04 ± 0.03	56.4 ± 0.9	123.4 ± 2.9	—
H	2.88 ± 0.01	4.82 ± 0.02	6.91 ± 0.03	8.82 ± 0.07	55.3 ± 0.5	126.3 ± 1.8	1.000
4'-Cl	6.33 ± 0.06	11.33 ± 0.45	16.48 ± 0.07	21.12 ± 0.07	59.6 ± 1.5	104.9 ± 5.0	—
4'-Br	6.72 ± 0.14	11.41 ± 0.65	16.89 ± 0.09	21.87 ± 0.07	58.6 ± 2.2	108.1 ± 7.7	—
4'-CN	15.09 ± 0.32	24.09 ± 0.52	32.97 ± 0.12	42.88 ± 0.20	51.5 ± 1.3	125.6 ± 4.5	—
4'-NO ₂	20.15 ± 0.11	33.00 ± 0.08	46.14 ± 0.21	59.87 ± 0.26	53.5 ± 0.4	116.2 ± 1.5	—
2'OMe	2.09 ± 0.02	3.75 ± 0.08	5.41 ± 0.08	7.49 ± 0.04	62.7 ± 1.3	103.7 ± 4.5	1.013
2'Me	2.56 ± 0.01	5.57 ± 0.13	7.90 ± 0.03	11.11 ± 0.07	71.5 ± 1.0	71.6 ± 3.3	1.286
2'-Cl	6.14 ± 0.01	12.66 ± 0.09	18.55 ± 0.17	25.17 ± 1.10	69.3 ± 1.6	72.0 ± 5.4	1.117
2'-F	9.24 ± 0.06	14.23 ± 0.38	19.17 ± 0.07	24.64 ± 0.12	47.7 ± 1.1	142.3 ± 3.7	—
2'-NO ₂	18.15 ± 0.54	30.72 ± 0.07	38.37 ± 0.01	52.13 ± 0.09	50.2 ± 0.9	127.5 ± 3.0	0.931

slow step to form complex (C) which decomposes to the epoxide in a fast step (Eq. 4) and subsequently the epoxide is cleaved through the attack of HOO⁻ ion (Eq. 5). In the epoxidation of mesityl oxide and ethylideneacetone by hydrogen peroxide, Bunton and Minkoff⁵ postulated that the epoxidation proceeded by a slow initial attack of HOO⁻ ion on the β-carbon atom followed by ring closure and elimination of OH⁻ ion from the adduct in a concerted manner. Temple⁶ reported cleavage of epoxide formed in the reaction of α,β-unsaturated ketone with alkaline hydrogen peroxide followed by retro-aldol reaction of α,β-unsaturated ketone by hydroxide ion. Cleavage of the present α,β-unsaturated system by hydroxide ion is ruled out based on the fact that no reaction occurred with hydroxide ion in the absence of H₂O₂.

The proposed mechanism is consistent with the experimental facts. The entropy of activation (Table 3) is negative as expected for a bimolecular rate-determining step with specific orientation of the reactants in the transition state.

Substituent effect

The rate data in Table 3 show that the rate is accelerated by electron-withdrawing and retarded by electron-releasing substituents. A good Hammett correlation is found to exist in the 4'-substituted N-methyl-2-styrylpyridinium iodide series, when log k_1 values are plotted against the σ_p constants. The result of the correlation is expressed by Eq. (6).

$$\log k_{30^\circ} = 0.916\sigma_p - 3.210 \quad \dots (6)$$

(± 0.064)

$$r = 0.988; s = 0.063; n = 7$$

The correlation is improved when multiple regression analysis is carried out using dual substituent parameter (DSP) equation (Eq. 7).

$$\log k_{30^\circ} = 1.075\sigma_I + 0.758\sigma_R - 3.278 \quad \dots (7)$$

(± 0.056) (± 0.063)

$$R = 0.997; SE = 0.036; n = 7; CL = 99.5\%$$

The F-test significance of the regression is 99.5% which shows that the correlation is meaningful. The t-test significance of the coefficients is above 90% indicating the significance of both the effects. The positive values of the regression coefficients indicate that a nucleophilic attack occurs on the substrate and that electron-withdrawing groups accelerate the reaction and electron-releasing groups retard it. The magnitudes of the regression coefficients suggest that the inductive effect is predominant over the resonance effect. The percentage of resonance effect⁷, P_R , is found to be 41.4.

The rate data of 2'-substituted N-methyl-2-styrylpyridinium iodides were analysed with Taft's linear free energy-steric energy relationships⁸. The results are expressed by Eqs (8) and (9). The values of σ_0^* and E_s involved in correlations were those given by Taft⁸.

$$\log k_{30^\circ} = 0.784\sigma_0^* - 3.228 \quad \dots (8)$$

$r = 0.992; s = 0.053; n = 5$

$$\log k_{30^\circ} = -0.427 E_s - 2.909 \quad \dots (9)$$

$$r = 0.764; s = 0.268; n = 5$$

The results show that the polar effect is important and the primary steric effect is insignificant. The ratio of the rate constants for similar *ortho*- and *para*-substituted benzene systems has also been taken as a measure of steric effect of the *ortho*-substituents⁹. The values of k_o/k_p are all more than one for all the substituents except the nitro group (Table 3). A poor correlation is obtained between $\log k_o/k_p$ and E_s (Eq. 10) which also indicates the minor role of the 'primary steric effect'.

$$\log \frac{k_o}{k_p} = 0.016 E_s + 0.031 \quad \dots (10)$$

$$r = 0.186; s = 0.072; n = 4$$

Charton's method⁷ was applied to the present rate data using Eqs (11) and (12)

$$\log k_o = \alpha \sigma_I + \beta \sigma_R + h \quad \dots (11)$$

$$\log k_o = \alpha \sigma_I + \beta \sigma_R + \phi v + h \quad \dots (12)$$

In Eqs (11) and (12), σ_I , σ_R and v are inductive, resonance and steric substituent constants and the values used were those compiled by Aslam *et al.*¹⁰.

Correlation analysis with Eqs (11) and (12) was performed and the results obtained are given in Eqs (12) and (13).

$$\log k_{30^\circ} = 1.138 \sigma_I + 0.681 \sigma_R - 3.248 \quad \dots (13)$$

$$(\pm 0.197) (\pm 0.228)$$

$$R = 0.962; SE = 0.123; n = 6; CL = 99.5\%$$

$$\log k_{30^\circ} = 1.113 \sigma_I + 0.708 \sigma_R + 0.170 v - 3.292$$

$$(\pm 0.32) (\pm 0.269) (\pm 0.336) \quad \dots (14)$$

$$R = 0.996; SE = 0.142; n = 6; SL = 99\%$$

The significance of the correlation tested by means of F-test shows that the above two correlations are meaningful. The confidence levels of the inductive and resonance terms obtained by means of the student t-test are above 95% showing that both the effects are significant. But the steric term is found to be insignificant as the confidence level based on student t-test is less than 90%.

The positive coefficients of σ_I and σ_R show that the electron-withdrawing substituents accelerate the rate of the reaction and electron-releasing substituents retard it. The value of P_R is estimated to be 37.4%. The value of P_R shows that the localised effect is more dominant than the delocalised effect and the delocalised effect is slightly more pronounced in the 4'-substituted series than in the 2'-substituted series.

Activation parameters

The activation parameters obtained (Table 3) are characteristic of bimolecular nucleophilic attack. The negative values of entropy of activation show the development of charge in the transition state. It is found that the ΔH^\ddagger values are slightly lower for 4'-substituted series as compared to the 2'-substituted series. The plot of ΔH^\ddagger versus ΔS^\ddagger is linear ($r = 0.962$) and the isokinetic temperature is found to be 325K. Exner plot^{11,12} of $\log k$ at 313K against $\log k$ at 298K is also linear ($r = 0.987$) and the value of isokinetic temperature is found to be 684K. Existence of good correlation implies that all the substituted compounds follow the same mechanism¹³.

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