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Oxidation of Styrylpyridinium Dyes by Permanganate Ion

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(Received April 28, 1994)

The oxidation of *N*-alkyl substituted styrylpyridinium bromides in both $KMnO_4$ and cetyltrimethylammonium permanganate (CTAP) results in the formation of corresponding substituted benzaldehydes. The oxidation in aqueous medium is catalyzed by acid whereas in chloroform medium the reaction proceeds at neutral condition. However, the reaction proceeds through the same mechanism in both the media. The faster rate of oxidation in aqueous medium by $KMnO_4$ than that in chloroform medium by CTAP has been rationalized through hydrophobic effect. The overall rate equation can be represented as rate=k[Substrate]$^{1.5}$[Oxidant]$^{-0.75}$ in aqueous medium and rate=k[Substrate]$^{0.5}$[Oxidant]$^{-1}$ in chloroform medium. From the substituent effect a transition state with low electron density at the olefinic carbon has been proposed.

Cyanine dyes play an important role in photosensitization. The use of these dyes in photofilms is more than a hundred years old. The dyes interact with different reagents during processing of photofilms, and undergo redox reactions. Due to the presence of a hydrophobic chain in the dyes, they show different behaviors in different environments.[1)] Sahay et al.[2)] have proposed the formation of a water-insoluble monolayer on water surface for these types of dyes and have investigated the permanganate oxidation of the monolayers.[3)] They have not, however, investigated the mechanism of oxidation in details.

In the present investigation a series of *N*-alkyl-4-styrylpyridinium dyes have been synthesized and their kinetics of oxidation have been investigated with $KMnO_4$ and cetyltrimethylammonium permanganate (CTAP).

Experimental

Materials. Potassium permanganate, perchloric acid, and sodium fluoride were of Anal R grade and were used without further purification. Acetic acid was of Merck grade and was purified by distilling it in presence of 2% potassium permanganate before use.[4)] Triple distilled water was used throughout the experiment.

Chloroform (Merck) was purified by suspending it with CTAP for 48 h, followed by fractional distillation from the mixture. It was redistilled just before each experiment.

CTAP was prepared by stirring cetyltrimethylammonium bromide with an equimolar amount of potassium permanganate in distilled water. A dark compound separated immediately which was washed with water several times. The yield was found to be 92%.

Styrylpyridinium dyes were synthesized by the condensation of *N*-alkyl-4-methylpyridinium bromide and aromatic aldehydes (Scheme 1). γ-Picoline and alkyl bromides were commercially available (SISCO) and were used after distillation at room temperature. Aromatic aldehydes were commercially available and were used without further purification. All the melting points were recorded by using a melting point apparatus and are reported uncorrected.

Synthesis of *N*-Butyl-4-methylpyridinium Bromide. A mixture of γ-picoline (0.02 mol) and butyl bromide (0.02 mol) was refluxed in a dry round bottom flask for 14 h at 120—140 °C on an oil bath. The resultant salt was washed with a solution of ether and acetone and was kept in a desiccator. The salts prepared by this method are from pentyl, octyl, and hexadecyl bromides.

Synthesis of *N*-Butyl-4-(*p*-methoxystyryl)pyridinium Bromide. *N*-Butyl-4-methylpyridinium bromide (0.01 mol) was dissolved in hot absolute ethanol (15 ml). To this solution, 2—3 drops of piperidine and anisaldehyde (0.01 mol) were added and the reaction mixture was refluxed for 3 h. A dark colored solution was obtained. The volume of the reaction mixture was then reduced under vacuum to a pasty mass. It was washed with diethyl ether till a colorless ether extract was obtained on washing. The residue was a dark colored solid mass which was then recrystallized from rectified spirit, mp 103 °C, yield: 75%. NMR values (in δ) 0.92 (3H, t), 1.35 (2H, t), 1.82 (2H, q), 4.3 (2H, t), 6.8 (1H, d), 7.56 (1H, d), 7.05 (1H, dd), 7.63 (1H, dd), 7.81 (1H, d), 8.38 (1H, d), and 2.88 (6H, s).

The compounds prepared by the above method, their mp, yield, and elemental analyses are given in Table 1.

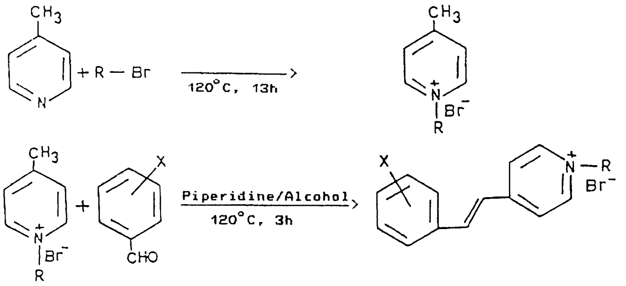
The compound 1-cetyl-4-(4-dimethylaminostyryl)pyridinium bromide was synthesized as reported earlier.[1)]

The purity of the compounds was checked on TLC plates by eluting in water–1-propanol–acetic acid medium.

Method of Rate Measurements. For the reaction in water medium the solutions of the dyes were made in

Table 1. Physical Constants of Styrylpyridinium Dyes and Their CH Analysis Data

Dye	Mp in °C	Yield (%)	%C (Calcd)	%H (Calcd)
1	103—105	65	62.2 (62.4)	6.1 (6.2)
2	>270	75	63.2 (63.3)	6.8 (6.8)
3	143—144	75	63.1 (63.1)	6.6 (6.5)
4	205—206	70	64.0 (64.1)	7.2 (7.1)
5	103—106	58	59.2 (59.0)	5.5 (5.6)
6	202—206	45	59.0 (59.1)	5.6 (5.6)
7	219—221	55	65.7 (66.0)	6.9 (6.8)
8	185—187	55	65.3 (65.4)	7.2 (7.3)
9	155—157	45	66.4 (66.3)	5.2 (5.4)
10	202—203	68	69.8 (70.0)	8.6 (8.8)
11	98—100	58	70.3 (70.4)	9.0 (9.1)
12	130	65	67.0 (67.0)	8.1 (8.2)
13	250	60	61.0 (61.2)	5.7 (5.8)



R	X	R	X	R	X
1. C_4H_9	*p*-OMe	**2.** C_4H_9	*p*-NMe_2	**3.** C_5H_{11}	*p*-OMe
4. C_5H_{11}	*p*-NMe_2	**5.** C_5H_{11}	*p*-Cl	**6.** C_5H_{11}	*o*-Cl
7. C_5H_{11}	*p*-Me	**8.** C_8H_{17}	*p*-OMe	**9.** C_8H_{17}	*p*-NMe_2
10. $C_{16}H_{33}$	*p*-OMe	**11.** $C_{16}H_{33}$	*p*-NMe_2	**12.** $C_{16}H_{33}$	*p*-Cl
13. C_3H_7	*p*-OMe				

Scheme 1.

20% acetic acid (1.6×10^{-3} M, 1 M=1 mol dm^{-3}), and the solution of $KMnO_4$ (2×10^{-3} M) was made in perchloric acid (0.4 M). Sodium fluoride (2×10^{-3} M) was used to suppress the formation of Mn (III) and Mn (IV). Permanganate was monitored at 526 nm.

For the reaction in chloroform medium, the solution of dyes and CTAP were prepared in chloroform and an aliquot of 0.04×10^{-3} M dye and 0.36×10^{-3} M CTAP were mixed in a quartz cell which was kept in a thermostated cell holder. Permanganate was monitored at four different wave lengths; 566, 544, 524, and 486 nm. A Hitachi-200 UV-vis spectrophotometer was used to study all the reactions in both aqueous and non-aqueous media. An MK-70 cryostat was used to maintain the temperatures (±0.1 °C).

Results

In the aqueous medium the first-order rate constants (k_Ψ) were calculated from the slopes of the linear plots of $\log(OD_o/OD_t)$ at 526 nm versus time. But in the nonaqueous medium, four different wavelengths, 566, 544, 524, and 486 nm were considered. The first order rate constants were calculated from the slopes of $\log(OD_o/OD_t)$ versus time for the dissipation of peaks at 566, 544, and 524 nm and $\log(OD_t/OD_o)$ versus time for the formation of the peak at 486 nm. The second-order rate constants (k_s) were obtained by dividing the first order rate constants by the concentration of substrates ($k_s=k_\Psi/[\text{Substrate}]$). Energy ($E_a$), enthalpy ($\Delta H^{\neq}$), and entropy of activation ($\Delta S^{\neq}$) have been calculated by using the Arrhenius and Eyring equations. First order rate data for the reactions in aqueous as well as in the nonaqueous media are presented in Tables 2 and 3 respectively.

The plots of $\ln k_s$ versus $1/T$ (where k_s is the second order rate constant) were linear in all cases.

The concentrations of sodium fluoride and acetic acid have no effect on the reaction rates in the aqueous medium. But increase in the concentration of perchloric acid increases the rates of the reaction. (Table 4).

The rate data obtained by varying the oxidant and substrate concentrations in aqueous medium have been summarized in Table 4. The plots of the logarithms of substrate and oxidant versus logarithms of first order rate constants were found to be linear with slopes 1.5 and −0.75 respectively (Fig. 1). In case of the reactions in the nonaqueous medium, first order dependence on the concentration of the oxidant and fractional order dependence on the concentration of the substrate is observed (Fig. 2).

The Hammett plot for oxidation of substituted styrylpyridinium dyes in the aqueous medium was found to be a curve whereas it was found to be a straight line in the nonaqueous medium (Fig. 3).

Sequential scans obtained during the oxidation in the nonaqueous medium have isosbestic points at 584 and 494 nm. This suggests that the reaction does not involve a complicated sequence of events as suggested by Jaky and Simandi.[5] Addition of cetyltrimethylammonium bromide (10^{-4}—10^{-3} M) to the reaction mixture was found to have no effect on the rate of oxidation reaction.

Product Analysis. Stilbenes[6] on oxidation with $KMnO_4$ yield diol. But the oxidation of styrylpyridinium dyes resulted in the cleavage of double bond with the formation of aldehydes in both the aqueous and

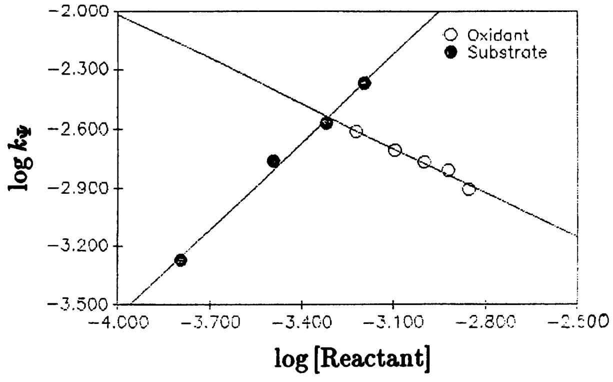


Fig. 1. Effect of Dye (**3**) and oxidant concentration on the first-order rate constants (k_Ψ) for the permanganate ion oxidation in water medium at 30 °C (r=0.99).

Table 2. First Order Rate Constants for the Oxidation of Styrylpyridinium Dyes (0.32×10^{-3} M) by Acid Permanganate (1×10^{-3} M) in Water Medium at 526 nm

	$k_\Psi\times10^5/\mathrm{s}^{-1}$				E_a	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$\Delta F^{\neq}$
Substrate	25 °C	30 °C	35 °C	40 °C	$\mathrm{kJ\,M^{-1}}$	$\mathrm{kJ\,M^{-1}}$	$\mathrm{kJ\,M^{-1}\,K^{-1}}$	$\mathrm{kJ\,M^{-1}}$
C_4–OMe	64.3	85.2	117.0	154.8	47.0	44.5	0.12	80.5
C_4–NMe_2	126.0	177.0	224.3	290.0	43.6	41.0	0.12	78.6
C_5–OMe	126.0	172.0	230.0	297.0	45.6	43.1	0.12	78.7
C_5–NMe_2	165.0	220.0	298.8	400.3	47.2	44.7	0.11	78.1
C_5–*p*Cl	49.0	67.0	86.1	124.8	48.7	46.2	0.12	81.1
C_5–*p*Me	46.2	60.8	84.0	113.3	47.9	45.4	0.12	81.3

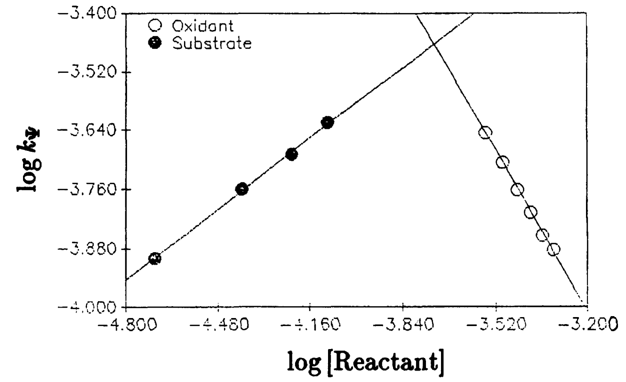


Fig. 2. Effect of Dye (**3**) and oxidant concentration on the first-order rate constants (k_Ψ) for the permanganate ion oxidation of styrylpyridinium dyes in chloroform medium at 30 °C (r=0.99).

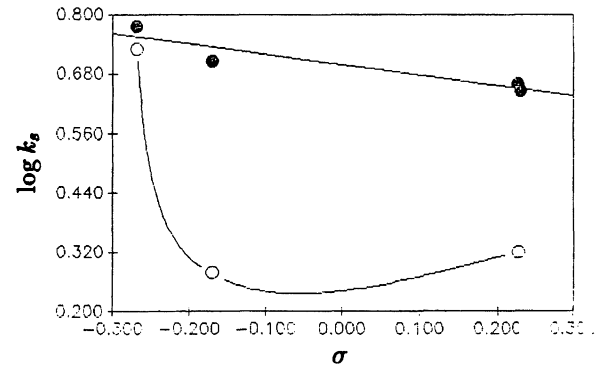


Fig. 3. Hammett plot for the oxidation of substituted styryl dyes by permanganate ion in water (○) medium ($[KMnO_4]=1\times10^{-3}$ M and $[\mathrm{Dye}]=0.32\times10^{-3}$ M) and in chloroform (●) medium ($[\mathrm{CTAP}]=0.36\times10^{-3}$ M and $[\mathrm{Dye}]=0.04\times10^{-3}$ M), Temperature=30.0±0.1 °C.

nonaqueous media.

Corresponding benzaldehydes have been isolated and characterized from their 2,4-dinitrophenylhydrazone derivatives. After filtering off the MnO_2 obtained at t_∞ (keeping the reaction mixture for 48 h), the ether or chloroform extract of the reaction mixture was dried and was subjected to carbonyl group test with 2,4-dinitrophenylhydrazine. It gave positive tests for the corresponding benzaldehydes. The water portion was also concentrated on a water bath and acidic 2,4-dinitrophenylhydrazine was added to it. No trace of hydrazone was obtained. It may be assumed that 4-formyl-*N*-alkylpyridinium bromide is adsorbed on the MnO_2 surface which is difficult to desorb either by the addition of alkali or acid.

Discussion

(i) Aqueous Medium. The second order rate constant is found to depend on the concentration of MnO_4^- and the substrate (Eqs. 1, 2, and 3).

$$\mathrm{Rate} = k_1[MnO_4^-] \tag{1}$$

$$= k_2[\mathrm{Substrate}] \tag{2}$$

$$= k_3[MnO_4^-][\mathrm{Substrate}] \tag{3}$$

Dependence of Perchloric Acid Concentration. To see the effect of $[H^+]$ on the oxidation of the styrylpyridinium dyes, the rate of oxidation with increasing $[H^+]$ has been studied with a representative dye, **3**. The hydrogen ion provided by $HClO_4$ is found to have a remarkable effect on the rate of oxidation of the dye. Banerji and Mathur[7)] have observed a hydrogen ion dependence of the rate of oxidation of diols by sodium *N*-bromobenzenesulphonamide and have proposed a mechanism involving an equilibrium between the protonated and the unprotonated species. They have further suggested that the protonated species reacts faster than the corresponding unprotonated species. Gupta et al.[8)] have also shown a higher reactivity of the protonated species over the unprotonated one.

The increase in the rate with an increase in $[H^+]$ in the present study may be due to the protonation of the MnO_4^- resulting in the formation of a more powerful oxidant, permanganic acid ($HMnO_4$).[9)] An equilibrium exists between permanganate ion and permanganic acid as,

$$H_3O^+ + [MnO_4^-] \rightleftharpoons HMnO_4 + H_2O \tag{4}$$

The rate enhancement due to $HMnO_4$ has also been observed in the oxidation of 2,2,2,-trifluoro-1,1-ethanediol (fluoral hydrate),[10)] amino acids,[11,12)] esters,[13)] and diols.[14)] A mechanism consistent with the observed results can be represented as

Table 3. First Order Rate Constants and Thermodynamic Parameters (At 30 °C) for the Oxidation of Styrylpyridinium Dyes (0.04×10^{-3} M) by CTAP (0.36×10^{-3} M) in Chloroform Medium

Substrate	λ	$k_\Psi\times10^5/\mathrm{s}^{-1}$				E_a	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$\Delta F^{\neq}$
	nm	25 °C	30 °C	35 °C	40 °C	kJ M^{-1}	kJ M^{-1}	kJ M^{-1} K^{-1}	kJ M^{-1}
C4–OMe	566	16.12	22.40	29.40	38.72	46.2	43.6	0.17	95.5
(**1**)	544	19.92	28.12	37.68	51.00	49.5	47.0	0.16	94.9
	524	15.60	20.20	27.38	36.40	45.3	42.8	0.17	95.7
	486	6.80	9.28	12.92	17.96	51.7	49.2	0.16	97.7
C4–NMe$_2$	566	13.72	18.88	26.52	37.60	53.6	51.1	0.15	95.9
(**2**)	544	18.20	25.24	37.12	50.32	54.7	52.2	0.14	95.2
	524	13.80	18.76	25.80	37.20	52.5	49.9	0.15	95.9
	486	5.72	8.12	10.88	15.20	51.3	48.8	0.16	98.0
C5–OMe	566	18.20	26.52	35.12	49.72	52.4	49.9	0.15	95.0
(**3**)	544	21.92	31.12	44.00	62.40	55.5	52.9	0.14	94.6
	524	17.33	23.92	33.80	47.12	53.3	50.8	0.15	95.3
	486	6.76	9.52	13.60	19.52	56.4	53.8	0.14	97.6
C5–NMe$_2$	566	14.40	19.32	27.08	37.56	51.2	48.7	0.16	95.8
(**4**)	544	18.00	24.88	35.72	51.00	55.5	53.0	0.14	95.2
	524	12.20	17.28	25.36	36.40	58.3	55.8	0.13	96.1
	486	5.92	7.40	9.52	12.32	39.1	36.5	0.20	98.2
C5–*p*Cl	566	15.20	19.52	27.12	33.72	43.3	40.8	0.18	95.8
(**5**)	544	19.12	24.80	32.52	44.92	45.1	42.6	0.17	95.2
	524	15.12	18.32	24.80	33.72	43.2	40.7	0.18	95.9
	486	7.80	10.00	13.00	17.00	41.4	38.9	0.19	97.5
C5–*o*Cl	566	15.00	17.96	22.20	27.20	31.8	29.3	0.22	96.0
(**6**)	544	18.60	22.28	27.20	33.40	31.4	28.9	0.22	95.5
	524	15.20	17.72	21.52	29.80	30.2	27.7	0.23	96.0
	486	4.04	6.52	10.52	17.60	77.9	75.4	0.08	98.6
C5–*p*Me	566	16.28	20.00	26.12	33.04	38.1	35.6	0.19	95.7
(**7**)	544	20.68	27.52	34.20	44.48	40.0	37.5	0.19	94.9
	524	16.68	20.32	26.32	32.04	35.3	32.8	0.21	95.7
	486	5.68	8.39	11.60	18.00	60.3	57.7	0.13	97.9
C8–OMe	566	17.20	25.12	30.96	39.92	43.5	40.9	0.18	95.2
(**8**)	544	21.00	31.20	39.52	52.60	47.6	45.0	0.16	94.6
	524	16.80	24.32	29.64	38.00	42.1	39.6	0.18	95.2
	486	5.72	7.80	12.52	18.32	63.2	60.7	0.12	98.1
C8–NMe$_2$	566	19.36	24.72	33.72	42.20	42.2	39.7	0.18	95.2
(**9**)	544	23.36	30.12	42.20	53.00	44.5	42.0	0.17	94.7
	524	17.96	23.40	30.48	40.00	42.5	39.9	0.18	95.3
	486	5.40	8.32	12.52	19.60	68.1	65.6	0.11	97.9
C16–OMe	566	17.28	21.16	27.40	33.40	35.6	33.1	0.21	95.6
(**10**)	544	20.88	25.00	33.68	42.32	38.6	36.0	0.19	95.2
	524	17.12	20.92	26.48	32.32	34.1	31.6	0.21	95.6
	486	5.40	6.72	8.39	10.52	35.4	32.9	0.22	98.5
C16–NMe$_2$	566	13.12	16.72	24.24	34.32	51.9	49.4	0.15	96.2
(**11**)	544	18.20	22.52	31.76	43.32	46.9	44.4	0.17	95.4
	524	12.32	16.52	23.04	31.80	50.6	48.1	0.16	96.2
	486	5.00	6.40	9.39	13.28	52.8	50.3	0.16	98.6
C16–*p*Cl	566	18.48	22.60	28.60	35.00	34.3	31.8	0.21	95.4
(**12**)	544	22.00	27.00	34.60	43.40	36.4	33.9	0.20	94.9
	524	18.20	21.92	27.68	33.68	33.1	30.6	0.21	95.5
	486	5.52	6.68	9.60	12.00	42.9	40.4	0.19	98.5
C3–OMe	566	16.76	20.22	25.12	32.52	35.3	32.8	0.21	95.7
(**13**)	544	19.00	24.00	31.00	40.32	40.0	37.5	0.19	95.3
	524	14.88	19.00	24.32	30.60	38.7	36.2	0.19	95.9
	486	4.72	6.88	9.60	13.68	56.1	53.6	0.15	98.4

$$\mathrm{H}^+ + \mathrm{MnO}_4^- \overset{K}{\rightleftarrows} \mathrm{HMnO}_4 \tag{5}$$

$$\mathrm{Dye} + \mathrm{MnO}_4^- \xrightarrow{K_1} \mathrm{P} \tag{6}$$

$$\mathrm{Dye} + \mathrm{HMnO}_4 \xrightarrow{K_2} \mathrm{P} + \mathrm{H}^+ \tag{7}$$

$$\mathrm{Rate} = k_1[\mathrm{MnO}_4^-][\mathrm{Dye}] + k_2[\mathrm{HMnO}_4][\mathrm{Dye}]$$

Table 4. Dependence of the Observed First Order Rate Constants on the Dye, Perchloric Acid, and Potassium Permanganate Concentrations (Temperature=30 °C)

Concentration of Reactants			$k_\Psi \times 10^5$
[Dye]	$[HClO_4]$	$[KMnO_4]$	s^{-1}
$\times 10^3$ M	M	$\times 10^3$ M	
0.16	0.4	1	52.9
0.32	0.4	1	172.0
0.48	0.4	1	271.0
0.64	0.4	1	419.0
0.32	0.1	1	85.2
0.32	0.2	1	119.0
0.32	0.3	1	147.0
0.32	0.5	1	218.0
0.32	0.6	1	276.0
0.32	0.4	0.6	246.0
0.32	0.4	0.8	195.0
0.32	0.4	1.2	154.0
0.32	0.4	1.4	124.0

$$= [\mathrm{Dye}]\{k_1[\mathrm{MnO_4^-}] + k_2K[\mathrm{H^+}][\mathrm{MnO_4^-}]\} \tag{8}$$

or,

$$\mathrm{Rate}/([\mathrm{Dye}][\mathrm{MnO_4^-}]) = k_1 + k_2K[\mathrm{H^+}]. \tag{9}$$

The plots of Rate/([Dye][MnO_4^-]) versus [H^+] is found to be a straight line with k_1 value to be 1640.6 s^{-1} and k_2K value to be 9968.8 $mol^{-1}\,s^{-1}$ (Fig. 4). The possibility of protonation of dye has been ruled out due to the fact that the dye is positively charged.

Variation of Rate with Substrate and Oxidant Concentrations. The rate of oxidation increase sharply with a change in the substrate concentration. The plot of [Substrate] versus rate is found to be linear ($r=0.99$) passing through origin. To check the order of the reaction, $\log k_\Psi$ has been plotted with log [Substrate] with a slope ≈ 1.5. But with increasing [Oxidant], the rate of reaction decreases. From the plot of $\log k_\Psi$ versus log [Oxidant], the order of reaction with respect to the oxidant is found to be -0.75 (Fig. 1). The data, further, have been subjected to multiple regression analysis and the overall rate equation can, thus, be represented as rate $= k[\mathrm{Substrate}]^{1.5}[\mathrm{Oxidant}]^{-0.75}$ where, $k=1.024$ $mol^{-1}\,s^{-1}$.

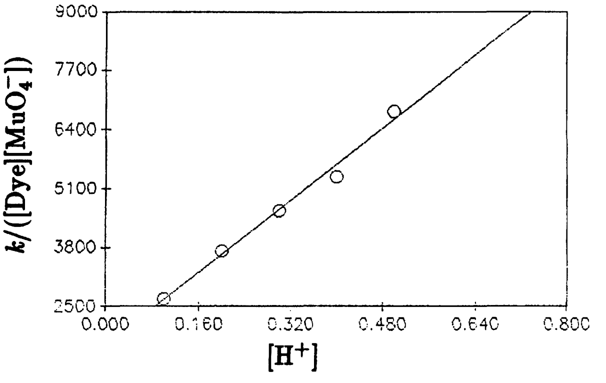


Fig. 4. Plot of hydrogen ion concentration ([H^+]) versus k_Ψ/([Substrate]/[Oxidant]) for the permanganate oxidation of styrylpyridinium dye (**3**) in water medium at 30 °C.

Effect of Substituent. Lee and Brown[15)] have proposed a mechanism for the oxidation of double bonds initially involving a charge transfer between olefinic double bond and MnO_4^-. Consequently, a charge is generated on the carbon having the double bond. While studying the mechanism of permanganate oxidation of cinnamate, they have proposed that a carbocation is generated on the carbon atom α to the carbonyl group of the ester. In the present study, the correlation of Hammett's substituent constants, σ, with $\log k_s$ is found to be nonlinear with a negative deviation indicating a transition state with low electron density in the benzene nucleus (Fig. 3). The possibility of the localization of the charge is either at the carbon α- to pyridinium ring or at the carbon β- to it as shown in Scheme 2.

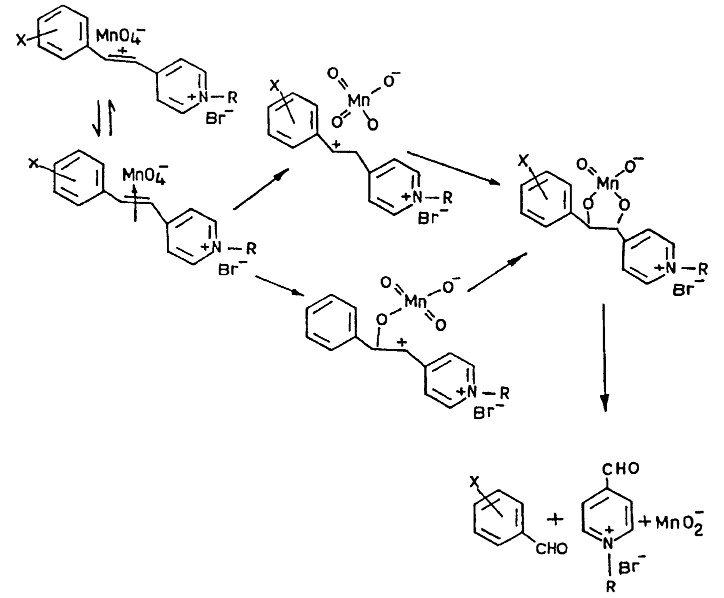
Effect of Temperature. A large negative entropy of activation (80—96 $J\,mol^{-1}\,K^{-1}$) indicates the involvement of a cyclic intermediate.[16)] With increasing chain length there is no significant change in $-\Delta S^{\neq}$ thus denying the probability of formation of aggregate during the oxidation process.

Effect of Chain Length. With an increase in alkyl chain, the hydrophobic character of the substrate increases and the solubility decreases. In the present study, the *N*-alkyl chains present in the pyridinium moiety are butyl and pentyl systems. Interestingly, dyes with pentyl chain react faster than those with butyl chain and the difference is also significant. This may be attributed to the differential inductive effect of alkyl chains on the pyridinium moiety towards the stability of the intermediate.

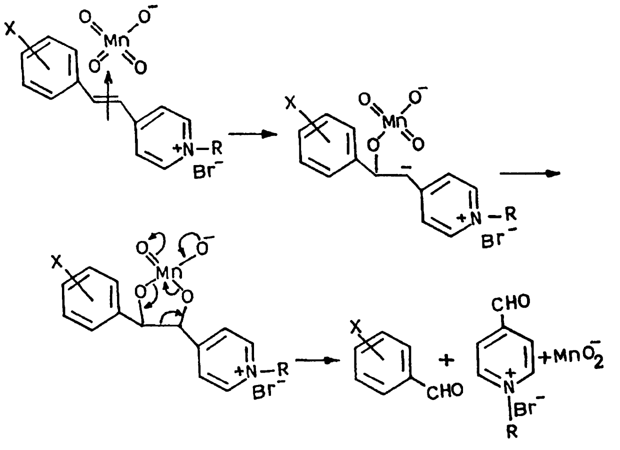
(ii) Nonaqueous Medium. From the product formed and the simplicity of the reaction inferred from the isosbestic points, it is clear that *N*-alkyl-4-styrylpyridinium dyes are oxidized by CTAP to yield corresponding aldehydes (Scheme 3).

The reaction takes place in a neutral condition and yields the same product as obtained in aqueous medium in acidic condition. Potassium permanganate in acidic condition forms permanganic acid which is responsible for the high reactivity of Mn (VII). Cetyltrimethylammonium permanganate forms a tight ion pair in nonpolar medium and because the substrate is also a charged one, both hydrophobic interaction as well as electrostatic effect bring the reactant and the substrate into proximity, thereby, facilitating the reaction.

Perez-Benito and Lee[17)] have observed a bell-shape plot for the reaction rate versus time and have suggested the participation of the product for catalytic action. They have also observed a straight line by plotting log (Absorbance) versus log (Wavelength) obtained from the reaction mixture after the reaction was



Scheme 2.



Scheme 3.

over. This happens when colloidal MnO_2 scatters light and satisfied Raleigh's law for light scattering.[18] In the present study, the plot of log (Wavelength) versus log (Absorbance) is found to be a curve (Fig. 5) and the plot of oxidation rate versus time was found to be a straight line (Fig. 6). These observations clearly suggest a noncatalytic reaction for the oxidation of *N*-alkyl-4-styrylpyridinium bromide with CTAP.

Effect of Substituent. The rates of oxidation of *N*-alkyl-4-(4-substituted styryl)pyridinium bromide determined at 524 nm were correlated (r=0.95) by a Hammett plot producing a reaction constant (ρ)=−0.21 (Fig. 3). Good straight line could not be obtained due to less number of data points and their varied positions in the benzene nucleus. Nothing can be said clearly from the ρ value thus obtained and about the transition state though the negative value of ρ indicates an electron deficient carbon center in the transition state.

Many workers have proposed an electron deficient center through a charge transfer intermediate, which generates an electron deficient center in the substrate.

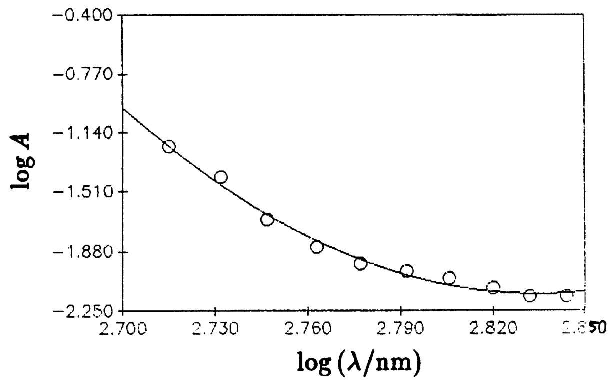


Fig. 5. Plot of log A versus log λ for the product formed from the reaction of styrylpyridinium dye, **3**, (0.04×10^{-3} M) with cetyltrimethylammonium permanganate (0.36×10^{-3} M) in chloroform at 30 °C.

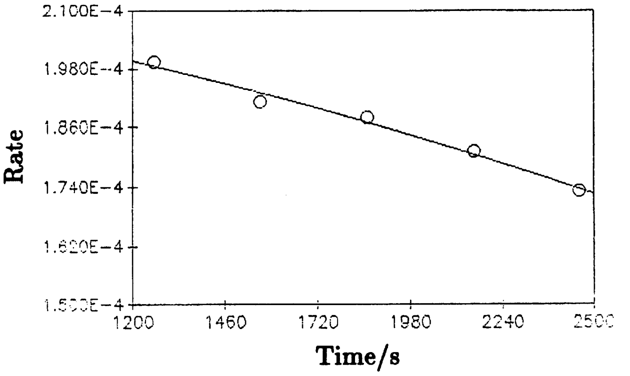


Fig. 6. Plot of first order rate (k_Ψ) versus time for the oxidation of styrylpyridinium dye (**3**) by CTAP at 30 °C.

Table 5. Dependence of the Observed First and Second Order Rate Constants (k_Ψ and k_s in s^{-1} and $mol^{-1}\,s^{-1}$ respectively) on the Dye Concentration for the Oxidation of Styrylpyridinium Dyes by CTAP in Chloroform Medium (Temperature=25°C, [CTAP]=0.36×10^{-3} M)

[Substrate]	566 nm		544 nm		524 nm		486 nm	
$\times10^3$ M	$k_\Psi\times10^5$	k_s	$k_\Psi\times10^5$	k_s	$k_\Psi\times10^5$	k_s	$k_\Psi\times10^5$	k_s
0.02	13.4	6.70	15.5	7.75	12.6	6.30	6.3	3.15
0.04	18.2	4.55	21.9	5.48	17.3	4.33	7.0	1.75
0.06	21.8	3.63	26.9	4.48	20.4	3.40	7.2	1.20
0.08	24.8	3.10	31.1	3.89	23.7	2.96	7.5	0.94

Table 6. Dependence of the Observed First and Second Order Rate Constant (k_Ψ and k_s in s^{-1} and $mol^{-1}\,s^{-1}$ respectively) on the CTAP Concentration for the Oxidation of Styrylpyridinium Dyes by CTAP in Chloroform Medium (Temperature=25°C, [Dye]=0.04×10^{-3} M)

[Oxidant]	566 nm		544 nm		524 nm		486 nm	
$\times10^3$ M	$k_\Psi\times10^5$	k_s	$k_\Psi\times10^5$	k_s	$k_\Psi\times10^5$	k_s	$k_\Psi\times10^5$	k_s
0.28	23.8	5.95	29.0	7.25	22.6	5.65	8.1	2.0
0.32	20.6	5.15	24.9	6.23	19.6	4.90	7.6	1.9
0.36	18.2	4.55	21.9	5.48	17.3	4.33	7.0	1.8
0.40	16.4	4.10	19.8	4.95	15.5	3.88	6.5	1.6
0.44	14.9	3.73	17.9	4.48	14.0	3.50	6.0	1.5
0.48	13.5	3.38	16.4	4.10	13.1	3.28	5.0	1.3

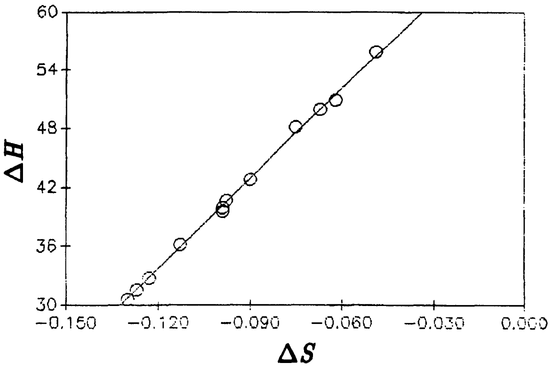


Fig. 7. Exner's plot for the oxidation of styrylpyridinium dyes by cetyltrimethylammonium permanganate in chloroform. [CTAP]=0.36×10^{-3} M, [Dye]=0.04×10^{-3} M; Temperature=30 °C. Slope= 305 °K, r=0.999.

In this study, the substrate has a net positive charge thus preferring a nucleophilic attack of the permanganate ion. This would lead to a neutral transition state (Scheme 3) with a quinonoid skeleton.

Attempts have been made to detect the transition state from the UV-vis spectra. The scanning of the reaction mixture with time shows clear isosbestic points and does not show any extra peak due to the intermediate. A probable mechanism for the reaction can be proposed as given in Scheme 3.

Effect of Substrate and Oxidant Concentrations. A representative dye (**3**) was chosen to see the effect of the substrate and oxidant concentrations on the rate of oxidation.

The rate increases with increasing the substrate concentration (Table 5). The plot of log [Substrate] versus log k_Ψ becomes a straight line with a slope ≈0.5 as shown in Fig. 2 (log [Substrate] versus log k_Ψ for 566, 544, and 524 nm have the slopes 0.444, 0.499, and 0.449 respectively; r=0.999). However, the rate decreases with increasing the oxidant concentration (Table 6). From the plot of log [Oxidant] versus log k_Ψ, the order of reaction with respect to [Oxidant] is found to be 1 as shown in Fig. 2 (the slopes obtained are −1.039, −1.042, and −1.029 for 566, 544, and 524 nm respectively; r=0.999). An overall rate equation, hence, can be proposed as:

$$\text{Rate} = k[\text{Substrate}]^{0.5}[\text{Oxidant}]^{-1} \qquad (10)$$

Thermodynamic Parameters. The activation parameters with respect to k_Ψ have been evaluated (Table 3). The negative entropy of activation indicates the presence of an ionic transition state as suggested by Stewart et al.[10,19] and Hassan et al.[20] Leffler and Grunwald[21] have pointed out that many reactions show an isokinetic relationship, $\Delta H^{\neq}=C+B\Delta S^{\neq}$. As shown in Fig. 7, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are found to be linearly correlated with an isokinetic temperature of 315 K. This linearity indicates that a similar type of mechanism must be occurring in the oxidation reaction for all the substrates.

Further, on analyzing the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values of p-methoxy and p-dimethylamino styrylpyridinium dyes with varying alkyl chain it has been observed that the thermodynamic parameters produce a maximum and a minimum respectively when plotted with the chain length. The values are found to be in between C_5–C_6 chain length. Clausse et al.[22] have suggested that the chain length of C_5 to C_6 in an alcohol or amine makes it a good co-surfactant to form microemulsion with other surfactants. The ΔH_f values for the alkanes, when plotted against chain length, also produce an optimum value at pentane.[23]

These observations support the participation of alkyl chains of the dyes during the oxidation reactions.

The authors thank Professor G. B. Behera for discussion and one of the authors (S.D.) thanks Sambalpur University for grating him a fellowship.

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