Kinetic Studies on the Oxidation of Orange–II by Cr(VI) in Absence and Presence of Micelle forming Surfactants

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Kinetic studies on the oxidation of Orange–II by Cr(VI) in acid medium revealed that the reaction is first order with respect to each of the reactants. Rate is also found to be proportional to hydrogen ion concentration. A mechanism consistent with the results for the cleavage of $-N=N-$ by the oxidant has been proposed. 0.02M concentration of Brij-35 inhibited the rate of oxidation by 10 times. Micelles of sodium dodecyl sulfate (SDS) have little effect on the rate. Micelles of cetyltrimethyl ammonium bromide (CTAB) so strongly inhibited the rate, that no appreciable change in the substrate concentration is detected in 2 hrs. Influence of surfactants on the rate has been discussed on the basis of the reaction mechanism and the interactions between the substrate and micelles. Analysis of Brij-35 effect on the basis of a model proposed to explain the micellar effects gave a value of $3.89 \times 10^{-4} s^{-1}$ for rate constant in micellar phase and $2.28 \times 10^{3} M^{-1}$ for micelle-substrate binding constant. Activation parameters for the reaction in absence and presence of surfactants have been compared.

INTRODUCTION

In the recent past, there have been number of reports on reactions occurring in presence of organised aggregates[1–3]. Micelle forming surfactants in aqueous medium have been found to cause significant rate enhancements and inhibitions of several organic and inorganic reactions[4–6]. However, there are very few reports on the electron transfer reactions in micellar systems[7]. With a view to understand the mechanism of oxidation of azo group by metal ions and to find the nature of interactions between azo dyes and micelles of different charge type, the kinetic study of oxidation of a widely used dye, 2–naphthol azobenzene p–sulphonic acid (Orange–II) by Cr(VI) in absence and presence of surfactants is undertaken. Though kinetics of oxidation of some aromatic azo compounds by Cr(VI), catalysed by oxalic acid has been reported[8], no attempt has been made to investigate the micellar effects on such reactions.

In this paper we report the kinetics of the decolorization of orange–II by Cr(VI) in acid medium and in presence of surfactants sodium dodecyl sulfate (SDS), polyoxy ethylene(23)–dodecanol (Brij–35) and cetyltrimethyl

ammonium bromide (CTAB). The finding that, the rate of oxidation of azo dyes is greatly inhibited in micellar environment may find practical utility in dyeing process.

EXPERIMENTAL

Orange–II has been prepared and recrystallized twice by reported method[9]. Cetyltrimethyl ammonium bromide and sodium dodecyl sulphate were purified by recrystallisation in the usual way[10,11]. Brij–35 obtained from Koch-Light laboratories was used without further purification. All the other materials used were of analytical grade reagents. Water was redistilled in glass vessels.

Kinetic measurements were carried out spectrophotometrically using Shimadzu-160A UV-Visible recording Spectrophotometer by observing decrease in absorbance of Orange-II at 484 nm as a function of time. Other species have negligible absorption at this wavelength. Ionic strength was maintained constant using potassium chloride. The cell containing reaction mixture was maintained at the desired temperature with a precision of $\pm 0.1°C$ by using a INSREF cryostatic bath, which circulated water around the cell holder jacket of the spectrophotometer. Calculations and analysis of the kinetic data was carried out using a DCM personal computer.

Products were extracted into ether and analysed by TLC using chloroform-methanol mixture as a solvent. Two spots were observed. The presence of nitroso groups in the compounds of both the spots were identified by the spot test prescribed by Feigl[12].

RESULTS AND DISCUSSION

Kinetic runs were carried out under psuedo first order conditions keeping the concentration of Cr(VI) 10 times greater than that of Orange-II. Plots of log absorbance versus time were found to be linear showing that the reaction is first order with respect to Orange-II. Such plots at different initial concentrations of Orange-II were found to be parallel. Pseudo first order rate constants obtained from the slopes of the plots are given in Table 1.

The values of rate constants determined at different Cr(VI) concentrations are listed in Table 1. Graph of rate constant vs Cr(VI) concentration is found to be linear passing through the origin indicating that the reaction is first order in oxidant (Fig. 1). Increase in H+ concentration is found to increase the rate of reaction linearly (Fig. 1) revealing the first order nature of the reaction with respect to H+. Increase in ionic strength slightly decreased the rate (Table 1).

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TABLE 1

EFFECT OF VARYING ORANGE–II, Cr(VI), H$^+$ CONCENTRATIONS
AND μ ON PSEUDO FIRST ORDER RATE CONSTANTS
FOR THE OXIDATION OF ORANGE-II BY Cr(VI)

[Orange–II]=4×10^{-5}M, [Cr(VI)]=4×10^{-4}M, [H$^+$]=0.05M, μ=0.06, Temp.=25°C

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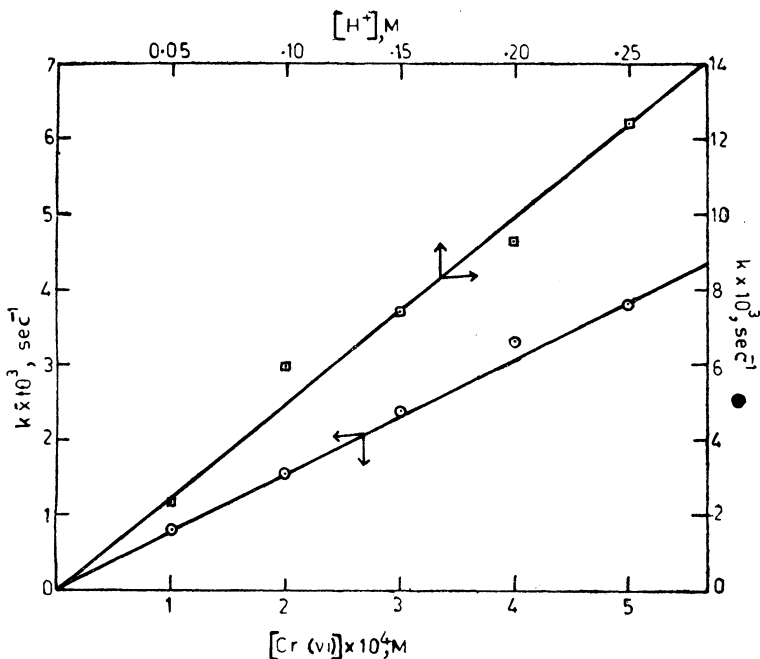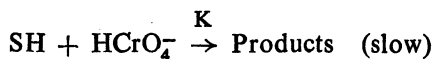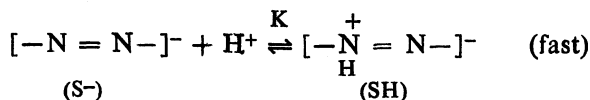| [Orange-II] × 10^5,M	k×10^3, sec^{-1}	[Cr(VI)] ×10^4,M	k×10^3, Sec^{-1}	[H$^+$], M	k×10^3, Sec^{-1}	μ	k×10^3, Sec^{-1}
1	3.23	1	0.81	0.05	2.18	0.05	3.36
2	3.36	2	1.55	0.1	6.04	0.1	3.09
3	3.39	3	2.37	0.15	7.45	0.15	2.72
4	3.29	4	3.33	0.2	9.30	0.20	2.39
5	3.26	5	3.84	0.25	12.40	0.25	2.28

Fig. 1. Plot showing variation of rate constant with Cr(VI) ⊙ and
hydrogen ion (|⋅|) concentration.

The following scheme of mechanism consistent with the above
results is proposed for the oxidation of −N=N− group of Orange-II by
Cr(VI) in acidic medium.

$$[-N = N-]^- + H^+ \overset{K}{\rightleftharpoons} [-\overset{+}{\underset{H}{N}} = N-]^- \quad \text{(fast)}$$

$$\text{(S}^-\text{)} \qquad\qquad\qquad \text{(SH)}$$

$$SH + HCrO_4^- \overset{K}{\rightarrow} \text{Products} \quad \text{(slow)}$$

$$\text{Scheme I}$$

According to the above scheme the rate of disappearance of Orange-II is given by the expression

$$\frac{-d[\text{Orange–II}]}{dt} = kK \, [\text{Orange–II}] \, [HCrO_4^-] \, [H^+] \tag{1}$$

Effect of Non-ionic Surfactant

Non-ionic surfactant Brij-35 inhibited the rate of oxidation of Orange–II by Cr(VI) in presence of 0.05M hydrogen ion concentration (Fig. 2). The data of variation of rate constant with Brij-35 concentration
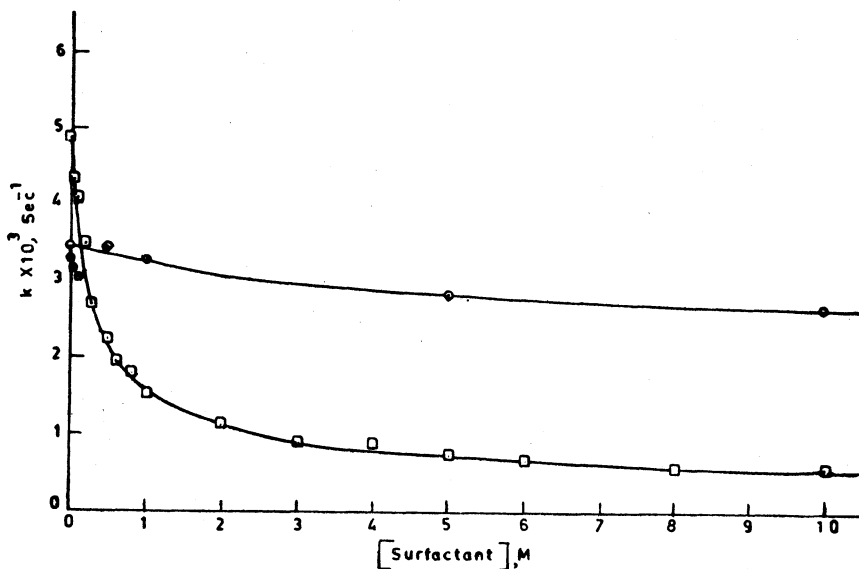

Fig. 2. Dependence of rate constant on surfactant concentration
        (|⁻₋|) Brij–35, (☉) SDS.

is given in Table 2. The inhibition is observed with Brij-35 concentration as low as 1×10^{-5}M, indicating that even premicellar aggregates also interact with the dipolar molecules of Orange-II (SH). Inhibition may
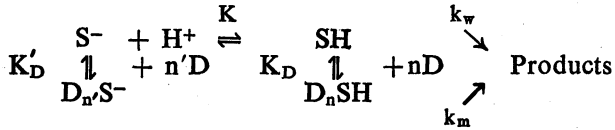
be the result of association of SH with non-ionic micellar and premicellar aggregates of Brij–35 causing the reaction site less available for the oxidation by Cr(VI). The extent of inhibition by 0.02M Brij–35 is about 10 times.

TABLE 2

EFFECT OF SURFACTANTS ON THE RATE OF OXIDATION OF
ORANGE–II BY Cr(VI)

[Orange-II] = 4×10^{-5}M; [Cr(VI)] = 4×10^{-4}M for SDS; [Cr(VI)] = 6.5×10^{-4}M
for Brij–35; [H$^+$] = 0.05M; μ = 0.06; Temp. = 25°C

$[C_D] \times 10^3$	SDS $k \times 10^3$, sec^{-1}	Brij–35 $k \times 10^3$, sec^{-1}
0	3.45	4.916
0.01	3.29	
0.05	3.16	4.361
0.1	3.07	4.113
0.2		3.504
0.3		2.728
0.5	3.45	2.255
0.6		1.932
0.8		1.843
1.0	3.33	1.533
2.0		1.160
3.0		0.920
4.0		0.875
5.0	2.88	0.748
6.0		0.696
8.0		0.610
10	2.71	0.581
15		0.494
20		0.436

To explain the inhibitory effect of Brij–35 and to analyse the data of variation of the observed rate constant (k_ψ) on Brij–35 concentration, the following model is proposed.

$$S^- + H^+ \underset{}{\overset{K}{\rightleftharpoons}} SH \overset{k_w}{\searrow}$$

$$K_D' \ \Updownarrow + n'D \qquad K_D \ \Updownarrow + nD \qquad \text{Products}$$

$$D_{n'}S^- \qquad\qquad D_nSH \qquad \nearrow$$

$$k_m$$

<div align="center">SCHEME 2</div>

This model, which is similar to that proposed by Bruice et al[13] and further used by Psizkiewicz[14] to analyse the micellar effects of several reactions, envisages that the protonated dye anion (SH) and n molecules of detergent D, aggregate to form D_nSH. Here, k_w and k_m are the rate constants of reaction in aqueous and micellar phases. K_D is the dissociation constant of the aggregate D_nSH. If favourable electrostatic forces between dye anion (S^-) and detergent ions exist, a number n′ of detergent ions will associate with S^- to form an ineffective $D_{n'}S^-$ aggregate. K_D' is the dissociation constant of the aggregate $D_{n'}S^-$. The fraction of SH bound to surfactant aggregates is shielded from the attack by the oxidant $HCrO_4^-$ and hence rate in this micellar psuedo phase would be very less. The observed rate, which includes the rates in aqueous and micellar phases gets reduced with increase in Brij–35 concentration, as more SH binds to Brij–35 aggregates.

Scheme 2 gives the following expression for k_Ψ where binding of SH to detergent aggregates is predominant and binding of S^- to the detergent aggregates is negligible.

$$k_\Psi = \frac{K_D k_w + k_m[D]^n}{K_D + [D]^n} \qquad (2)$$

Rearrangement of the above expression gives :

$$\log\left[\frac{k_\Psi - k_w}{k_m - k_\Psi}\right] = n \ \log[\bar{D}] - \log K_D \qquad (3)$$

As required by equation 3, plot of log $(k_\Psi - k_w/k_m - k_\Psi)$ against log $[\bar{D}]$ for Brij–35 inhibited reaction is found to be linear (Fig. 3). A value of 1.03 for n obtained from slope of the plot reflects positive cooperativity[14] and indicates the existence of multiple equilibria in the formation of premicellar inhibitory aggregates of SH and Brij–35 detergent molecules.

Estimation of k_m

The observed rate constant for the Brij–35 inhibited reaction continued to decrease with increase in the Brij–35 concentration even at very high concentrations (Table 2). In order to estimate the rate of the reaction in micellar phase, k_m is calculated by applying the model proposed by Menger and Portnoy[15]. Expression for the observed rate constant according this model is given by
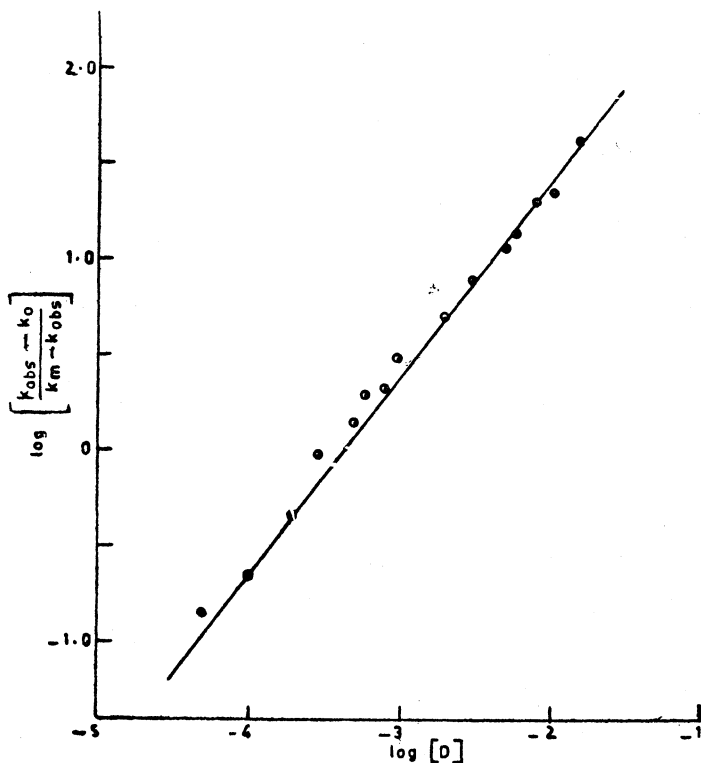
Fig. 3. Analysis of the effect of Brij-35 on the oxidation of Orange-II by Cr(VI)

$$\frac{1}{k_w - k_\Psi} = \frac{1}{k_w - k_m} + \frac{1}{k_w - k_m} \times \frac{N}{K_M([D] - cmc)} \qquad (4)$$

Here, K_M is the binding constant between substrate and micelle, N is aggregation number of the micelle and cmc is the critical micelle concentration. A reported cmc value of 1×10^{-4}M Brij-35 is used in this analysis[16]. The data at higher concentrations of Brij-35 (2×10^{-3}M to 2×10^{-2}M), where most of the detergent exist in aggregate form is analysed using equation 4. A plot of $1/(k_w - k_\Psi)$ against $1/([D] - cmc)$ is found to be linear as required by the model (correlation coefficient : 0.9921), k_m calculated from the intercept is found to be 3.89×10^{-4} s^{-1}. In the analysis of the data according to equation 3 this k_m value is used. A value of 2.28×10^3 for $\frac{K_M}{N}$ is obtained from the plot. This value indicates the existence of strong binding between the substrate and micellized detergent.

Effect of cationic surfactant :

Progressive addition of cationic surfactant CTAB to a solution of

4×10^{-4}M Cr(VI) in 0.05M H$^+$ at 25°C causes precipitation of CTAHCrO$_4$. But this precipitate gets solubilized in higher concentrations of CTAB and at 0.01M CTAB clear solution is obtained. Oxidation of Orange–II in presence of 0.01M CTAB is very strongly inhibited. Change in absorbance of the dye after 2 hrs is found to be very little. Rate constant estimated on the basis of this small change is found to be 3.84×10^{-6} sec^{-1} amounting to an inhibitory effect of about 900 times. This near total inhibition of the reaction is a clear example of specific interactions between micellar aggregates and substrate. Inhibition can be attributed to the incorporation of hydrophobically and electrostatically favourable interaction of dye anion (S$^-$) with cationic micelles of CTAB. This substantially decreases the concentration of the reactive protonated species SH and hence causes the inhibition.

Effect of Anionic Surfactant :

Anionic surfactant SDS has very little effect on the rate of oxidation of Orange–II (Fig. 2). The data of variation of rate constants with SDS concentration is given in Table 2. Due to unfavourable electrostatic interactions between dye anion (S$^-$) and anionic micellar aggregates, the reaction primarily takes place in the aqueous bulk phase and hence the rate is not altered appreciably. Little inhibitory effect (1.3 times in 0.01M SDS) may be due to weak interaction between dipolar dye molecule (SH) and SDS micelles and unapproachability of the HCrO$_4^-$ to this fraction of the dye.

Temperature effect in absence and presence of surfactants :

The plots of log k vs 1/T for the oxidation of Orange–II in absence and presence of 0·01M SDS, Brij–35 and CTAB have been found to be linear (Fig. 4). Activation energies and activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ calculated from the plots are given in Table 3. Increased values of activation energy in presence of surfactants as compared to those in absence are consistent with the fact that the reaction is inhibited in all the three types of surfactants. Strong inhibition in presence of CTAB can be interpreted in terms of an increase of about 6 K.Cal mole^{-1} activation energy in spite of relatively favourable entropy of activation. Inhibition of about 10 times in Brij–35 can be understood in terms of unfavourable entropy of activation. Little inhibitory effect in presence of SDS may be due to the opposing contributions of E$_a$ and $\Delta S^{\neq}$ factors. Large negative values of activation entropy indicate that more ordered activated complex is formed. Nearly same values of $\Delta G^{\neq}$ in absence and presence of surfactants show that similar mechanism for oxidation is operative in aqueous and micellar environment and the
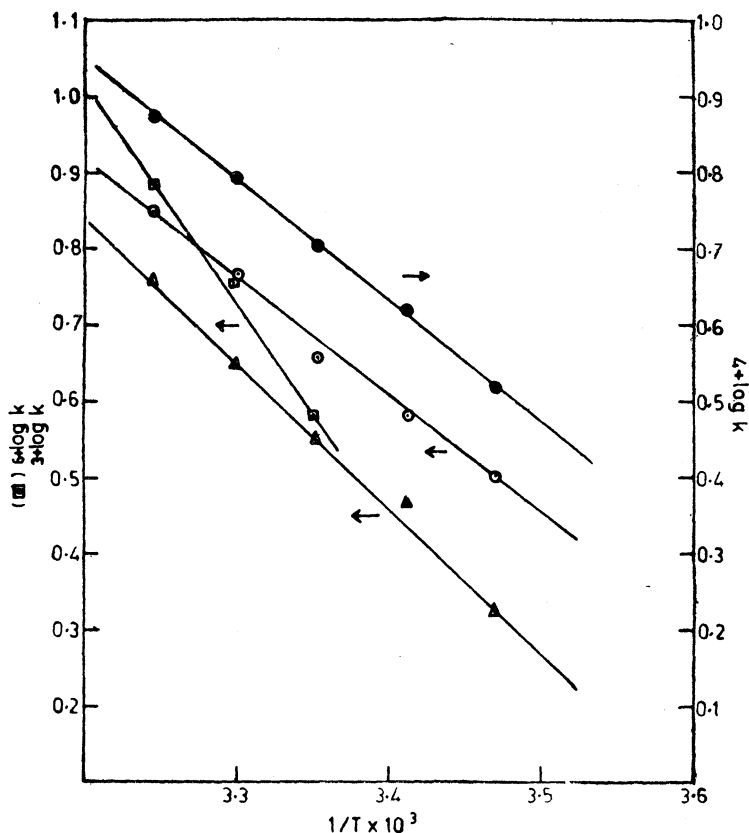
Fig. 4. Arrhenius plots for the oxidation of Orange-II in the absence and presence of surfactants. ($\odot$) no surfactant ($\triangle$) SDS, ($\boxminus$) CTAB, ($\bullet$) Brij-35.

TABLE 3

THERMODYNAMIC QUANTITIES OF ACTIVATION FOR THE OXIDATION OF ORANGE-II BY Cr(VI) IN PRESENCE AND ABSENCE OF SURFACTANTS

[Orange-II] = 4×10^{-5}M, [Cr(VI) = 4×10^{-4}M, [H$^+$] = 0.05M, [SDS] = 0.01M, [CTABr] = 0.01M, [Brij-35] = 0.01M, μ = 0.06, Temp. = 25°C.

Activation parameters	No Surfactant	SDS	Brij–35	CTABr
E$^{\neq}$, k. Cal mole^{-1}	6.86	9.15	7.02	12.81
A, lit mole^{-3}sec^{-1}	4.99×10^2	1.85×10^4	0.71×10^4	1.46×10^4
ΔG$^{\neq}$, k. Cal mole^{-1}	20.63	20.77	21.93	24.58
ΔS$^{\neq}$, Cal mole^{-1} deg^{-1}	−46.19	−39.00	−50.06	−39.48
ΔH$^{\neq}$, k. Cal. mole^{-1}	6.87	9.15	7.02	12.82

rate determining step is bimolecular. The values are also consistent with the occurrence of fast protonation equilibrium prior to rate determining step.

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REFERENCES

1. J. H. Fendler, Membrane Mimetic Chemistry, Wiley-Interscience, New York (1982).

2. ——, *Annu. Rev. Phys. Chem.*, **35**, 137 (1984).

3. E. H. Cordes and C. Gitler, *Prog. Biorg. Chem.*, **2**, 1 (1973).

4. J. H. Fendler and E. J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York (1975).

5. I. A. K. Reddy and S. S. Katiyar, *Tetrahedron*, **37**, 585 (1981).

6. C. A. Bunton, *Catal. Rev. Sci. Eng.*, **20**, 1 (1979).

7. C. A. Bunton and G. Cerichelli, *Int. J. Chem. Kinetics*, **12**, 519 (1980).

8. P. V. Subba Rao, K. S. Murthy; P. S. H. Murthy and R. V. S. Murthy, *J. Indian Chem. Soc.*, **56**, 604 (1979).

9. A. I. Vogel, Practical Organic Chemistry including Qualitative Organic Analysis, Longmans Green, London, p. 625 (1968).

10. E. F. J. Duynstee and E. Grunwald, *J. Am. Chem. Soc.*, **81**, 4540 (1959).

11. J. H. Cho and Morawetz, *J. Am. Chem. Soc.*, **94**, 375 (1972).

12. F. Feigl, Spot Tests in Organic Analysis, Elsevier, Pub. Co., p. 290 (1966).

13. T. C. Bruice, J. Katzhendler and L. R. Fedor, *J. Am. Chem. Soc.*, **90**, 1333 (1968),

14. D. Psizkiewicz, *J. Am. Chem. Soc.*, **99**, 1550 (1977).

15. F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.*, **89**, 4698 (1967).

16. P. Becher and N. K. Clifton, *J. Colloid Sci.*, **14**, 519 (1959).