

## Micellar Effect on the Reaction of Acid Green-16 with $K_2S_2O_8$ Ion: Influence of Salts and Organic Solvents

HITENDRA M. JOSHI and T.N. NAGAR\*

*Department of Chemistry, South Gujarat University, Surat -95 007, India*

Cationic micelles of cetyl trimethyl ammonium bromide ( $C_{16}TABr$ ) increase the rate of reaction of triphenylmethyl carbonium ions with  $S_2O_8^{2-}$  ion whereas the anionic micelles of sodium dodecyl sulphate (SDS) inhibit this rate. The addition of monohydric alcohols, viz., *n*-butanol, ethanol and solvents like acetone and dimethylformamide decreases the cationic micellar catalysed rate, while on the other hand increases the anionic micellar inhibited rate. The influence of electrolytes in the presence of  $C_{16}TABr$  has also been analysed.

**Key Words:** Micellar effect, Acid green-16, Potassium peroxydisulphate.

### INTRODUCTION

Organic reactions in aqueous surfactants undergo either rate acceleration or inhibition and this behaviour has been attributed to electrostatic and hydrophobic interactions between the substrate and surfactant aggregates. Some investigations on the influence of organic solvents on the micelle catalyzed inhibited reactions have been reported<sup>1-4</sup>. The effect of neutral salts on MG-peroxydisulphate<sup>5</sup> reaction has been reported. We have earlier studied the influence of salts and organic solvents on acid violet-49 in micellar environment<sup>6</sup>. The effect of organic solvents and salts on aqueous polymerization of acrylonitrile by persulphate-disulphite<sup>7</sup> redox system have been studied. In this paper, we report the effect of various organic solvents and electrolytes on the kinetic reaction of acid green-16 and  $K_2S_2O_8$  in presence of ionic surfactants.

### EXPERIMENTAL

Acid green-16 (AG-16) was purified before use<sup>8</sup>. The cationic surfactant cetyl trimethyl ammonium bromide ( $C_{16}TABr$ ) and anionic surfactant sodium dodecyl sulphate (SDS) were of Sigma Chemicals. Solvents like acetone, DMF, ethanol and *n*-butanol were of BDH analytical grade chemicals and were purified prior to use by standard procedure<sup>9</sup>. All the inorganic salts, viz., KCl, KBr,  $KNO_3$ ,  $K_2SO_4$  and NaCl were of BDH, AnalaR grade and used without further purification.

### RESULTS AND DISCUSSION

**Effect of solvents on the  $C_{16}TABr$  catalysed reaction of triphenylmethyl carbonium ions by  $K_2S_2O_8$  at 30°C**

The effect of various solvents on the oxidation reaction of AG-16 with

$K_2S_2O_8$  was investigated at fixed concentration of  $C_{16}TABr$  ( $2.0 \times 10^{-5}$  M) which in each case was much above the saturation concentration of surfactant in the rate vs. [surfactant] concentration profile<sup>10,11</sup>. The rate constant increases with the increase in the concentration of  $C_{16}TABr$ . Similar behaviour has been observed for malachite green and brilliant green dyes by  $K_2S_2O_8$ .<sup>12</sup> The kinetic data for the effect of solvents on the oxidation of AG-16 in micellar media are summarised in Table-1. Similar effect of various solvents on the oxidation reaction of carbonium ions was investigated at fixed  $[C_{16}TABr]$  and in each case the rate constant decreases with increase in percentage concentration of the solvents<sup>10,11</sup>.

TABLE-1  
PSEUDO FIRST ORDER RATE CONSTANTS AT VARYING CONCENTRATION OF ORGANIC SOLVENTS IN PRESENCE OF  $C_{16}TABr$  CATALYZED OXIDATION OF ACID GREEN-16 BY POTASSIUM PEROXYDISULPHATE AT 30°C.

[Acid Green-16] =  $2.5 \times 10^{-5}$  M [ $K_2S_2O_8$ ] = 0.005 M [ $C_{16}TABr$ ] =  $2.0 \times 10^{-5}$  M

Solvent % (v/v)	$k_{obs} \text{ min}^{-1}$			
	Ethanol	<i>n</i> -Butanol	DMF	Acetone
0.00	0.0575	0.0575	0.0575	0.0575
4.00	0.0309	0.0284	0.0268	0.0345
5.00	0.0268	0.0255	0.0251	0.0244
6.00	0.0223	0.0193	0.0230	0.0230
8.00	0.0183	0.0174	0.0153	0.0115
10.0	0.0172	0.0155	0.0148	0.0115
15.0	0.0172	0.0152	0.0148	0.0115

It may be seen from these data that the addition of acetone, DMF, ethanol and *n*-butanol to the reaction system reduces the overall catalysis by  $C_{16}TABr$ . It may be noted that *n*-butanol is more effective than ethanol in reducing the overall catalysis of these reactions by  $C_{16}TABr$ . The order of effectiveness of solvents is as follows:

acetone > DMF > *n*-butanol > ethanol

Several factors might be visualized which could explain the observed effects of solvents on chemical reactions in micellar media. Bruice and Cordes<sup>4</sup> have interpreted the effect of alcohols on the reaction of methyl benzoate with  $H^+$  ion in the presence of sodium dodecyl sulphate (SDS) by considering the following factors: (i) replacement of the substrate by solvent molecules from the micellar phase, (ii) changes in the aggregation properties of the surfactant and (iii) modification in the electrostatic stabilization of the transition state of the reaction in the presence of solvents.

It may be pointed out that the idea concerning the solvent effects on chemical reactivity have undergone drastic amendments since the classical concept of

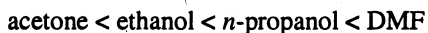
solvent as a continuous dielectric medium<sup>13-15</sup>. Evidences indicate that the selective solvation of the reactant and the motion of the solvent species constitute an important and integral part of the motion of reacting species along the reaction coordinates at the transition state. This is particularly true for ionic reactions. As a result of the accompanying motion of solvent molecules, the energy required to remove a solvent molecule from a reaction site to make space for an approaching reactant or to reorganize the solvent molecules as a function of the change in the charge distribution may have significant contribution to the activation energy and entropy in many reactions. It has been reported that the presence of solvent in the micellar media may have the effect of modifying or completely destroying the micelles<sup>16</sup>.

The alcohol molecules continuously exchange between aqueous and micellar phase and the extent of distribution depends upon the chain length of alcohols. When the single amphiphile is transferred into an aggregate, the water structure can become more disorganized giving rise to an increase in entropy. In addition, the attractive dipole-dipole interactions are re-established between water molecules. Thus the overall effect of solvents on chemical reactions in micellar media involved competitive as well as compensatory phenomena.

#### **Effect of organic solvents on the SDS inhibited oxidation reaction by $K_2S_2O_8$ with AG-16**

The influence of organic solvents, *viz.*, acetone, DMF, ethanol and *n*-butanol on the SDS inhibition reaction of AG-16 was investigated at fixed concentration of [surfactant], [reactant] and the [substrate] while varying the solvent composition in the reaction system. The studies were performed in each case at fixed [SDS] which corresponded to saturation concentration ( $3.0 \times 10^{-3}$  M) of the surfactant in the rate *vs.* [surfactant] profile for these reactions. It has been noticed that reaction rate decreases as the concentration of the SDS micelle increases<sup>12</sup>.

The results for the oxidation of AG-16 are graphically presented in Fig. 1. It may be observed from these kinetic data that the addition of solvents to micelle affected reaction markedly diminishes the overall inhibition caused due to the presence of SDS. The effectiveness of an alcohol to reduce the extent of overall inhibition is found to increase with the increasing carbon chain length of alcohol molecules. The order of effectiveness of solvents is as follows:



However, in the aqueous media with low percentage of the solvents, *viz.*, acetone, DMF and alcohols the reaction rate is retarded with increasing solvent percentage in the reaction system<sup>15,17</sup>. This observation eliminates the displacement of the substrate from micellar phase to the bulk phase. Complete destruction of catalytic micelle by solvents may also be ruled out, in the presence of solvents. The electrostatic as well as hydrophobic interactions among the species present in the reaction system would continue to exist, and also the concentration of solvents in the reaction system is too low to cause such effects. It appears more probable that some reorganization in the structure of catalytic micelles might

take place. In the formation of new catalytic aggregates, substrate, surfactant and solvent molecule might participate resulting in reorganization of reactant concentration at the reaction sites and a modification in the thermodynamic parameters of the reactions, which is manifested in diminishing the effectiveness of SDS on the reaction rate. Breaking of water molecules and consequent destabilization and selective solvation of reactants plays an important role in affecting the rate.

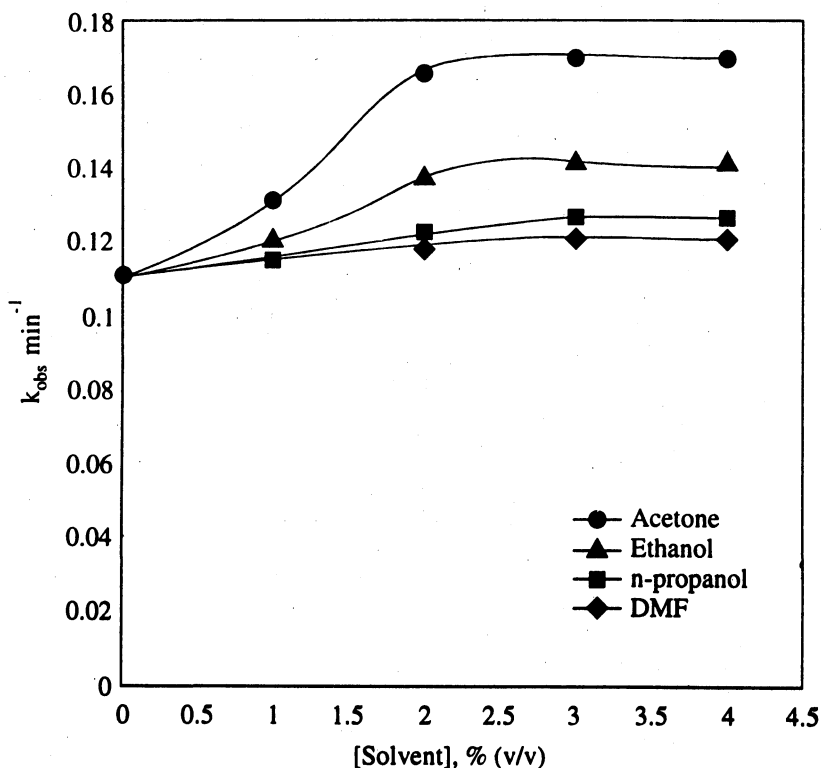


Fig. 1. Influence of organic solvents on SDS inhibited oxidation of Acid Green-16 by  $K_2S_2O_8$  at 30 °C. [Acid Green-16 =  $2.5 \times 10^{-5}$  M;  $[K_2S_2O_8] = 2.25 \times 10^{-2}$  M; [SDS =  $3.0 \times 10^{-3}$  M

#### Effect of added electrolytes on the $C_{16}TBr$ catalysed reaction of acid green-16 by $K_2S_2O_8$ at 30°C

The rate constant of the  $C_{16}TBr$  catalysed [ $2.0 \times 10^{-5}$  M] reaction in presence of added salts *viz.*, KCl, KBr,  $KNO_3$ ,  $K_2SO_4$  and NaCl are tabulated in Table-2. It is found that the rate constant decreases with increase in salt concentration of the anion.

It is also found that initially rate decreases and becomes almost constant at 0.1 M concentration of salts for the substrate. The rate of retardation with respect to anion follows the order:  $SO_4^{2-} > Br^- > NO_3^- > Cl^- > \text{no salt}$ .

TABLE-2  
PSEUDO FIRST ORDER RATE CONSTANTS AT VARYING CONCENTRATION OF  
ELECTROLYTES IN PRESENCE OF  $C_{16}TABr$  CATALYSED OXIDATION OF ACID  
GREEN-16 BY POTASSIUM PEROXYDISULPHATE AT 30°C

[Acid green-16] =  $2.5 \times 10^{-5}$  M;  $[K_2S_2O_8]$  = 0.005 M;  $[C_{16}TABr]$  =  $2.0 \times 10^{-5}$  M

[Salt], M	$k_{obs}$ (min <sup>-1</sup> )				
	NaCl	KCl	KNO <sub>3</sub>	KBr	K <sub>2</sub> SO <sub>4</sub>
0.00	0.0575	0.0575	0.0575	0.0575	0.0575
0.02	0.0518	0.0471	0.0425	0.0413	0.0383
0.04	0.0460	0.0441	0.0380	0.0331	0.0326
0.06	0.0413	0.0369	0.0350	0.0320	0.0309
0.08	0.0374	0.0321	0.0310	0.0279	0.0261
0.10	0.0333	0.0310	0.0309	0.0265	0.0253
0.12	0.0331	0.0310	0.0309	0.0265	0.0253
0.15	0.0328	0.0310	0.0308	0.0265	0.0253

This behaviour can be rationalized by assuming competition between  $S_2O_8^{2-}$  and the anion for the bonding site in the micelle. This phenomenon is explicable in terms of greater affinity of the low charge density anions for the micelle<sup>18</sup>

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