

## Micellar catalysed oxidative cyclisation of 1,3,5-triaryl formazan

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**Abstract.** The kinetics of Tl(III) acetate oxidation of 1,3,5-triaryl formazan has been studied in 90% aqueous HOAc, in the presence of added anionic detergent, sodium-lauryl sulphate (NaLS) and cationic detergent, cetyltrimethylammonium bromide (CTAB). Both surfactants enhance the reaction rate, indicating that the reactive species involved is possibly neutral. From the substituent influence observed in the micellar phase Hammett correlations have been attempted. Higher negative  $\rho$  values obtained in the presence of CTAB, indicate that the transition state is more electron-deficient. The positive co-operativity calculated for the micellar catalysed reactions (3.0) indicates possible hydrophobic interaction between micelle and formazan.

**Keywords.** Micellar catalysis; oxidative cyclisation; positive co-operativity.

### 1. Introduction

The oxidative cyclisation of formazan to a tetrazolium salt by several oxidants such as fuming nitric acid, lead tetra-acetate and molecular bromine, has been studied in detail. However, the mechanism of this reaction is not clear although cyclisation in the presence of molecular bromine has been assumed to involve an electrophilic attack by bromine at the carbon (Hegarty *et al* 1975).

The present study is about the effect of added cationic and anionic detergents on Tl(III) acetate oxidation of 1,3,5-triaryl formazan. The reactions were carried out in 90% HOAc-10% H<sub>2</sub>O mixture and these were so patterned that a structure-activity correlation can be attempted in the micellar phase and compared with the specific rates obtained in the absence of surfactants (Balakrishnan *et al* 1981).

### 2. Results and discussion

Micellar catalysis on the Tl(III) acetate oxidation of 1,3,5-triaryl formazan has been investigated in binary solvent mixture of acetic acid-water in the presence of surfactants of concentration above their cmc values.

#### 2.1 Rate dependence on the concentration of Tl(III) and 1,3,5-triaryl formazan

Table 1 summarises the results on the rate dependence on the substrate

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**Table 1.** Dependence of rate on the concentration of reactants.  
 [NaCl] = 0.010 M, Solvent = aq. 90% HOAc, temp. = 50°C, [surfactant] =  $6.0 \times 10^{-4}$  M

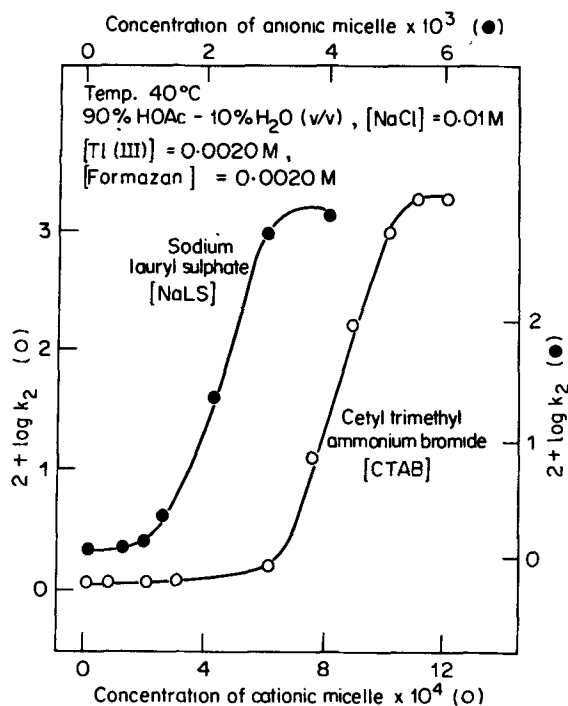
	[Tl(III)] M $\times 10^3$	[Formazan] M $\times 10^3$	$k_2 \times 10$ litre-mole <sup>-1</sup> sec <sup>-1</sup>
(a)	2	2	31
	2	4	30
	2	5	32
	4	5	31
	5	5	31
(b)	2	2	18.3
	2	4	18.6
	2	5	18.3
	4	5	18.5

(a) in CTAB; (b) in NaLS

concentration. The reaction exhibits total second order kinetics – first order with respect to each reactant – in the presence of added surfactants and this is similar to the behaviour observed in the absence of detergents.

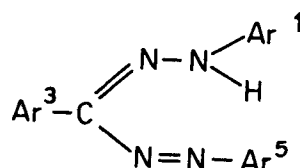
### 2.2 Rate dependence on detergent concentration

The effect of changing the concentration of the anionic micelle, sodium



lauryl-sulphate (NaLS), on the rate of Tl(III) acetate oxidation of 1,3,5-triaryl formazan has been investigated in the range  $6 \times 10^{-4}\text{M}$  to  $3 \times 10^{-3}\text{M}$  whereas the influence of cationic micelle, cetyltrimethylammonium bromide (CTAB) on the rate has been investigated in the range  $7 \times 10^{-5}\text{M}$  to  $1 \times 10^{-3}\text{M}$ . In both cases, the plot of  $\log k_2$  versus detergent concentration is sigmoidal (figure 1). As both cationic and anionic micelles act as positive catalyst for the reaction, the reactive Tl(III) species involved is possibly neutral. Beyond certain detergent concentration, there is an abnormal increase in rate, probably due to the change in micellar structure.

### 2.3 Substituent effect in the presence of micelle



In the presence of added detergent, either anionic or cationic, the oxidation rate of 1,3,5-triaryl formazan is susceptible to polar effects of substituents present in the phenyl rings  $\text{Ar}^1$ ,  $\text{Ar}^3$  and  $\text{Ar}^5$ . Table 2 summarises the data on the influence of substituents on the oxidation rate in the presence of NaLS and CTAB respectively. In both cases, electron withdrawing substituents like

**Table 2.** Substituent effect on the rate of oxidation in the presence of surfactants.  $[\text{NaCl}] = 0.01\text{M}$ , Solvent = aq. 90% HOAc, temp. =  $50^\circ\text{C}$ ,  $[\text{Tl(III)}] = 0.0020\text{M}$

Substituents	$\text{Ar}^1$		$k_2 \text{ M}^{-1} \text{ s}^{-1}$		$\text{Ar}^3$	
	<i>a</i>	<i>b</i>	$\text{Ar}^2$	<i>b</i>	<i>a</i>	<i>b</i>
H	18.3	31	18.3	31	18.3	31
<i>p</i> -methoxy	—	—	27	63	—	—
<i>p</i> -methyl	—	—	29	41	28	46
<i>m</i> -bromo	—	—	6.7	11.2	—	—
<i>m</i> -nitro	—	—	4.2	—	—	—
<i>o</i> -nitro	4.2	7.9	2.9	3.0	4.0	—
<i>p</i> -bromo	—	—	—	—	—	1.53
<i>o</i> -fluoro	—	—	10.2	16.3	—	1.13
<i>p</i> -iodo	—	—	—	—	11.3	—
<i>m</i> -chloro	9.3	—	—	—	8.3	—
2,4-dinitro	1.09	1.66	—	—	—	—
4-nitro	4.4	4.1	—	—	—	0.61
<i>p</i> -chloro	—	—	—	—	—	1.18

(a)  $[\text{NaLS}] = 6.0 \times 10^{-4}\text{M}$ ; (b) in  $[\text{CTAB}] = 6.0 \times 10^{-4}\text{M}$

**Table 3.** Hammett reaction constant ( $\rho$ ) values.  
NaCl = 0.01M, Solvent = aq.90% HOAc.

	substituents in		
	Ar <sup>1</sup>	Ar <sup>3</sup>	Ar <sup>5</sup>
(a) in the absence of micelle	-0.81 (0.9613)	-0.74 (0.9564)	-0.75 (0.9911)
(b) in the presence of NaLS	-0.83 (0.9973)	-0.94 (0.9935)	-0.82 (0.9929)
(c) in the presence of CTAB	-0.79 (0.9652)	-1.11 (0.9929)	-1.01 (0.9920)

In parentheses, the correlation coefficients are indicated

**Table 4.** Solvent influence.

[Tl(III)] = 0.0020M, [NaLS] =  $6 \times 10^{-4}$ M, [CTAB] =  $6 \times 10^{-4}$ M, temp. 55°C,  
[NaCl] = 0.0020M, [Formazan] = 0.0020M.

Solvent composition % HOAc - % H <sub>2</sub> O	$k_2 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$	
	(anionic) NaLS	(cationic) CTAB
90 - 10	23	38
80 - 20	28	47
70 - 30	31	54

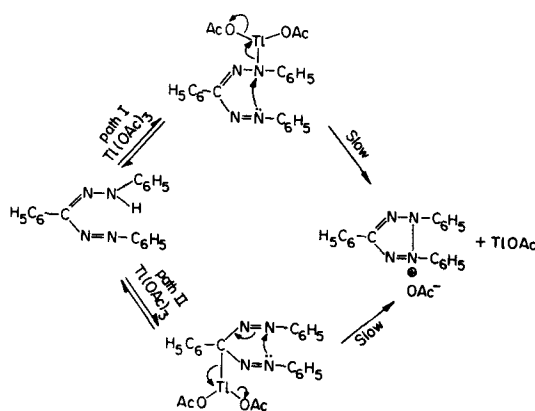
*m*-NO<sub>2</sub>, *o*-NO<sub>2</sub> in the phenyl rings Ar<sup>1</sup>, Ar<sup>3</sup> and Ar<sup>5</sup> retard the reaction rate whereas electron donating substituent enhance the reaction rate. Plots of log  $k_2$  versus substituent constants ( $\sigma/\sigma^+/\sigma_0$ ) are all linear and table 3 summarises the  $\rho$  values (slopes of the plots) obtained in the presence and absence of micelles. The negative  $\rho$  value indicates an electron-deficient transition state both in the presence and absence of micelle. The cationic micelle, CTAB seems to influence the rate markedly (as revealed by higher negative  $\rho$  value in this medium) indicating that the transition state is more electron-deficient in the micellar phase. Similar observations have been made in the acid-catalysed hydrolysis of a series of para-substituted methyl orthobenzoates by many workers (Romsted *et al* 1967; Fulligton and Cordes 1964; Behme *et al* 1965; Baumcker *et al* 1973; Dunlap and Cordes 1968, 1969).

#### 2.4 Solvent influence

With increasing polarity of solvent, there is an increase in rate in the presence of both anionic and cationic micellar-catalysed Tl(III) oxidative cyclisation of 1,3,5-triaryl formazan (table 4).

#### 2.5 Temperature influence

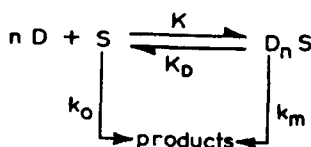
The temperature influence on these reactions has been studied in the range



Scheme 1

40 to 60°C and from the plots of  $\log k_2$  versus  $1/T$ , the activation energies have been calculated. Heats and entropies of activation are then derived and these are given in table 5. The higher negative entropy of activation indicates highly ordered transition state (scheme 1).

### 3. Co-operativity model for micellar-catalysed reaction



Scheme 2

S=substrate; D = detergent molecules;  $k_m$  and  $k_o$  are the rate constants in the micellar and aqueous phases respectively;  $K_D$  = dissociation constant of the micelle. According to scheme 2 (Piszkievicz 1977), the observed rate constant for the reaction can be given as

$$k_{\text{obs}} = \frac{k_m[D]^n - k_o K_D}{K_D + [D]^n}$$

which on rearrangement in logarithmic form becomes,

$$\log \frac{(k_{\text{obs}} - k_o)}{(k_m - k_{\text{obs}})} = n \log [D] - \log K_D.$$

The suggested linear plot of  $\log \{(k_{\text{obs}} - k_o)/(k_m - k_{\text{obs}})\}$  versus  $\log [D]$  is

**Table 5.** Arrhenius dependence.

Substituents	$E_a$ (i)	$\Delta H^\ddagger$ (ii)	$\Delta S^\ddagger$ (iii)	$\Delta G^\ddagger$ (iv)
(a) H in Ar <sup>1</sup>	11.9	10.6	-28	19.7
2,4-dinitro	11.9	11.3	-32	22
4-nitro	11.2	10.6	-32	21
in Ar <sup>3</sup>				
<i>p</i> -methyl	11.4	10.8	-27	19.5
<i>o</i> -nitro	11.3	10.7	-33	21
<i>m</i> -nitro	11.2	10.6	-32	21
in Ar <sup>5</sup>				
<i>p</i> -bromo	11.6	10.9	-29	20
<i>p</i> -chloro	11.4	10.7	-29	20
(b) H in Ar <sup>1</sup>	11.7	11.0	-28	20
4-nitro	11.6	10.9	-31	21
2,4-dinitro	12.2	11.6	-32	22
in Ar <sup>3</sup>				
<i>o</i> -nitro	11.3	10.6	-33	21
<i>m</i> -nitro	11.4	10.8	-32	21
<i>p</i> -bromo	11.0	10.4	-31	20
in Ar <sup>5</sup>				
<i>o</i> -nitro	10.9	10.3	-30	19.9

(a) CTAB (b) NaLS; (i) k.cal/mole; (ii) k.cal/mole; (iii) cal/mole/deg; (iv) k.cal/mole.

realised in the present investigation in both anionic and cationic micelles (figure 2) with slope  $n$  referred to as co-operativity index. The value of  $n$  is 3.1 in NaLS (correlation coefficient 0.97) and 2.9 in CTAB (correlation coefficient 0.95). As the  $n$  value is greater than 1, it is referred to as positive co-operativity. This indicates a stimulation of the association of additional detergent molecules to an aggregate as a result of the interaction with first detergent molecule. This kind of hydrophobic interaction between micelle and substrate may account for the enhancement rate observed in these media. Similar positive co-operativity is also encountered in the chlorination of anilines (Raghavan *et al* 1980) and phenols (Rengarajan *et al* 1980) by chloramine-T in the presence of NaLS.

#### 4. Experimental

1,3,5-triaryl formazans were prepared from the respective benzaldehyde, aniline and phenylhydrazine following the procedure cited in an earlier paper (Balakrishnan *et al* 1981). Acetic acid A R grade was refluxed with chromic anhydride at least three times before use. The surfactants, NaLS and CTAB, were repeatedly washed with anhydrous ether and recrystallised several times either from ethanol or methanol with the addition of anhydrous ether

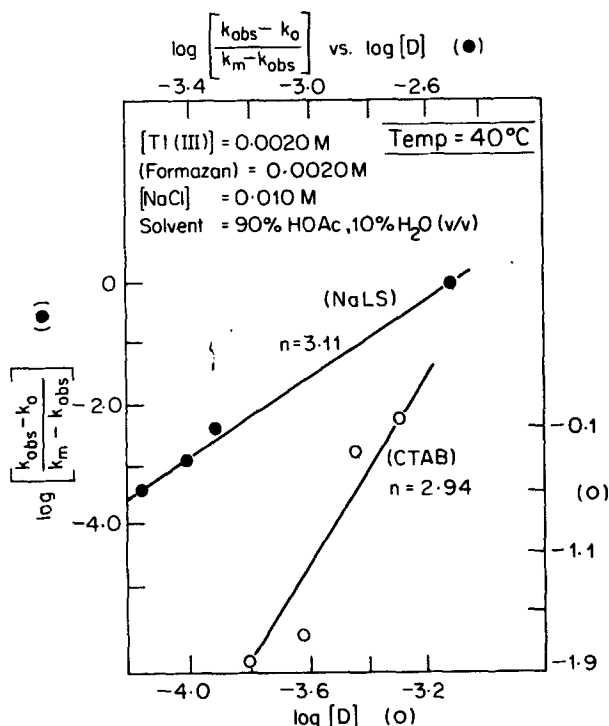


Figure 2.

or from water until the critical micelle concentration (CMC) remains constant (Fendler and Fendler 1975).

The CMC values under the present conditions (in 0.010 M NaCl and 90% HOAc) were determined for NaLS by using pararosaniline dye at  $630 \text{ m}\mu$  and for CTAB by using eosin dye at  $540 \text{ m}\mu$ . The values are found to be  $6 \times 10^{-4} \text{ M}$  and  $4.5 \times 10^{-5} \text{ M}$  respectively and these differ from CMC values obtained in aqueous medium by a factor of 10. The stoichiometry of the reaction, in the presence and absence of added surfactants, has been found to be 1:1 {[Tl(III)]: [1,3,5-triaryl formazan]}. The kinetics of the reaction has been monitored by estimating the unreacted Tl(III) iodometrically.

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