

Facile chlorination of acetophenone by chloramine-T in the cationic micellar phase

P S RAGHAVAN and VANGALUR S SRINIVASAN*

Department of Chemistry, Ramakrishna Mission, Vivekananda College, Mylapore, Madras 600 004, India.

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Abstract. The chlorination of acetophenone by chloramine-T (CAT) has been catalysed by added detergents, sodium laurylsulphate (NaLS) and cetyltrimethylammonium bromide (CTAB). Phenacyl chloride is the exclusive product of the reaction and the % yield of the product is greater in the cationic micellar phase indicating facile chlorination in this media (even in the absence of the mineral acid). Using Piskiewicz's treatment, the positive cooperativity for the micellar catalysed reactions has been calculated. At the cationic micellar phase of CTAB, the interaction between ammonium ion and phenyl and methylene groups probably leads to greater stabilisation than the simple hydrophobic association encountered in the micelle interior of NaLS.

Keywords. Chlorination of ketone; chloramine-T; micellar phase; mineral acid.

1. Introduction

Chlorination of reactive aromatic substrates such as cresols by chloramine-T (CAT) has been studied by several workers (Pryde and Soper 1931; Balasubramanian and Thiagarajan 1976; Higuchi and Hussain 1967). Although ketone chlorination (including acetophenone) has already been studied (Balasubramanian and Thiagarajan 1976), the present work attempts to delineate the nature of the transition state and the stabilising forces responsible for higher yield of chlorinated product, phenacyl chloride, in micellar phase.

2. Results and discussion

2.1 Rate dependence on [CAT] and [acetophenone]

The rate dependence on CAT has been determined by varying the initial concentration of CAT keeping the other parameters the same. The rate of disappearance of CAT follows first order kinetics both in the presence and absence of detergents (table 1). The reaction rate depends on [acetophenone] at lower concentrations but at higher concentrations, it becomes independent of [substrate]. In the presence of CTAB, the rate drops with increasing [acetophenone], attaining a minimum at higher concentrations. A similar decrease in rate with increasing [substrate] has been observed by Behme *et al* (1965) in the hydrolysis of methyl orthobenzoate in the presence of sodium dodecylsulphate. The decreasing rate with increasing substrate concentration most likely represents satur-

* To whom all correspondence should be addressed.

Table 1. Rate dependence on [CAT] and [acetophenone].

10 ³ [CAT]M	10 ² [Acetophenone]M	10 ⁵ k _{obs} s ⁻¹		
		a	b	c
1.5	4	—	5.5	—
2	4	—	5.8	—
4	4	—	5.7	—
2	0.8	—	2.3	—
2	1	—	2.8	—
2	1.5	—	4.2	—
2	2	1.97	5.5	46
2	3	2.7	5.6	42
2	4	3.7	5.8	22
2	5	4.0	5.6	21
2	7	—	—	23
2	8	—	—	21
2	10	—	5.9	—

(a) in the absence of detergents in 50% HOAc, in the absence of HClO₄ at 35°C. (b) in the presence of [NaLS] = 8 × 10⁻³ M in 20% HOAc 80% HOAcH₂O (v/v) containing 0.2 M HClO₄ at 30°C. (c) in the presence of [CTAB] = 8 × 10⁻⁴ M in 50% HOAc 50% H₂O (v/v) in the absence of HClO₄ at 35°C.

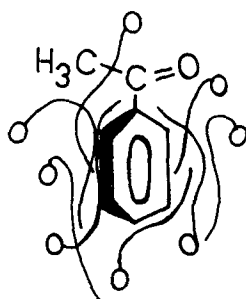
ation of the micellar phase with substrate. Thus, as substrate concentration increases beyond the saturation point, an increasing amount of the substrate must exist free in the solution. As this fraction approaches unity, the rate constant for the reaction must approach that for the reaction in purely aqueous solution and hence the observed decrease in rate.

2.2 Rate dependence on detergent concentration

Tables 2 and 3 summarise the influence of detergents, NaLS and CTAB, on the chlorination rate of acetophenone. The enhancement in rate observed is greater beyond 0.01 M NaLS, which appears to be the CMC of the detergent in the presence of reactants which is difficult to measure. This underscores the necessity of micelles in catalysing these reactions. Similar catalyses by NaLS have been observed in the chlorination of anilines (Raghavan *et al* 1980) and phenols (Rengarajan *et al* 1980) by CAT.

In the cationic micellar phase, even in the absence of mineral acid (in the absence of both mineral acid and CTAB, the rate of chlorination is very slow), the rate acceleration observed is considerable at the CTAB concentration of 4 × 10⁻⁴ M. The reasons for the enhanced catalysis by CTAB may be manifold. The cationic micellar phase may favour enolisation considerably. Also the solubility of acetophenone in CTAB is about 2 times greater than the solubility in NaLS and the ratio of acetophenone concentration in CTAB surfactant to water varies from 19.1 to 10.5 at 23°C when the surfactant is varied from CTAB to NaLS (Fendler *et al* 1975). As the incorporation of acetophenone is greater on the hydrophobic patches (Menger *et al* 1981) where CAT and water are available, catalysis seems to be significant in CTAB than in NaLS. Also the solubilisation site of acetophenone in cationic and anionic surfactants is most likely

near the surface or in the head group region (Balasubramanian *et al* 1982), but the aromatic ring and methyl group are oriented towards the interior and the carbonyl oxygen towards the surface as shown in scheme 1 (Fendler *et al* 1975).



Scheme 1. Schematic representation of general solubilisation sites of acetophenone in aqueous micellar solution.

Table 2. Rate dependence on NaLS concentration.

10^3 [NaLS]M	$10^5 k_{\text{obs}} \text{sec}^{-1}$
—	5.3
4	5.4
6	5.6
10	5.5
15	5.8
20	6.2
50	7.2
60	7.8
100	9.5

[acetophenone] = 4×10^{-2} M; [CAT]
= 2×10^{-3} M; [HClO₄] = 0.2 M; temp.
= 30°C; solvent: 20% HOAc—80%
H₂O.

Table 3. Rate dependence on CTAB concentration.

10^4 [CTAB]M	$10^5 k_{\text{obs}} \text{sec}^{-1}$
—	1.97
2	1.65
3	1.78
4	3.5
6	10
8	46
9	66
10	72

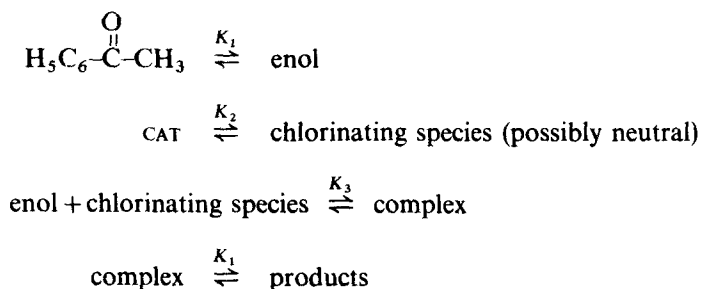
[acetophenone] = 2×10^{-2} M; [CAT]
= 2×10^{-3} M; temp. 35°C; solvent:
50% HOAc—50% H₂O.

As acetophenone penetrates to a greater extent in NaLS (Fendler *et al* 1975) than in CTAB, the halogenation by CAT present at the Stern layer probably becomes difficult. NMR results by Mueller (1973) confirm the progressive displacement of water from the outer core by the organic compound, affecting unequally the signals of different protons of CTAB. Along with the stabilisation of -C=O group by hydrogen bonding near the surface, both phenyl and methylene groups may interact with ammonium ion distant from the surface. This may give greater stability in CTAB than the simple hydrophobic association normally encountered in the micelle interior of NaLS.

Using Piskiewicz's treatment (1977) for the micellar-catalysed reaction, the co-operativity index n calculated equals 1.11 for NaLS catalysed reaction (Raghunathan *et al* 1982) and 5.2 for the CTAB-catalysed reaction. In both cases the n value (> 1) indicates the positive co-operativity or in other words, favourable substrate-micelle interactions, a factor which seems to be responsible for the observed catalyses. This is also in keeping with the facile chlorination in the presence of cationic surfactant.

3. Mechanism of chlorination of acetophenone

The fractional order dependence observed suggests that this reaction probably proceeds *via* the intermediacy of a complex formed between substrate and CAT, exhibiting Michaelis-Menton type of kinetics. This is explained by considering the following reaction sequence:



From the reaction sequence, we derive,

$$\text{rate} = \frac{K[\text{CAT}][\text{acetophenone}]}{1 + K'[\text{acetophenone}]},$$

where K and K' are the composites of K_1 , K_2 , K_3 and k_1 . At lower concentration of acetophenone, the decomposition of the complex seems to be the rate-determining step, exhibiting a fractional order dependence on acetophenone concentration. At higher concentrations, the formation of active species from CAT being the rate-determining step, a zero order dependence on acetophenone has been observed. As both, anionic and cationic micelles catalyse the reaction, the chlorinating species involved is probably neutral in nature.

4. Experimental

All the detergents used were of pure variety (BDH/Aldrich). The detergents were further purified by the procedure of Duynstee and Grunwald (1959) CAT [Societe des usines

Table 4. Stoichiometry.

[CAT]M	[Substrate]M	[CAT]:[Acetophenone]
0.01 ^a	0.002	0.0018:0.002
	0.004	0.0040:0.004
0.01 ^b	0.002	0.0020:0.002
	0.004	0.0042:0.004
0.01 ^c	0.002	0.0019:0.002
	0.004	0.0038:0.004

(a) in the absence of detergent; (b) in the presence of 0.01 M NaLS; (c) in the presence of 0.001 M CTAB.

chimiques Rhone-Boulene (Paris)] was used as such and its purity (> 99%) was ascertained by iodometric procedure. The other chemicals employed were of reagent grade and used as such after checking their physical constants.

The critical micelle concentration (CMC) of the surfactants was measured spectrophotometrically using dye as probes. The course of the reaction was followed iodometrically. The pseudo first-order rate constants were evaluated from the slopes of regression lines of $\log(b-x)$ vs time. The linear regression was analysed on a micro 2200 programmable calculator (Hindustan Computers).

4.1 Stoichiometry

The stoichiometry for the chlorination of acetophenone both in the presence and absence of detergents, was 1:1 (table 4). The stoichiometric experiments were performed with CAT in excess.

4.2 Product analysis

The products were analysed in the presence as well as absence of detergents. In both cases, phenacyl chloride has been identified as the product. The typical procedure employed to analyse the chlorinated product formed from acetophenone was as follows. Acetophenone (100 mmol, 20 ml) was mixed with CAT (50 mmol, 20 ml) in the presence of 0.5 M HClO₄ (10 ml) in 20% aqueous acetic acid. After the completion of reaction the acid was neutralised and the organic materials were ether extracted. The solvent was then distilled under vacuum and the product mixture chromatographed through a silica column. The product identified was phenacyl chloride (m.p. 56°C). The above procedure was repeated in the presence of CTAB and NaLS of different concentrations in the absence of HClO₄. After the reaction, the detergent was precipitated by adding 0.5 M KI solution and filtered. The rest of the procedure is the same as above. Table 5 summarises the yield of phenacyl chloride in the presence and absence of detergents. The yield is greater (in the absence of HClO₄) in the cationic micellar phase (in the absence of both mineral acid and detergent, chlorination does not occur).

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Table 5. Yield of phenacyl chloride in the presence and absence of detergents.

[Detergent] M	% [Phenacyl chloride]
0	2
0.001 ^a	29
0.002 ^a	58
0.01 ^b	13.6
0.02 ^b	19.4

[CAT] = 1×10^{-3} M; [acetophenone] = 1×10^{-3} M; temp. 30°C; Solvent = 20% HOAc—80% H₂O. (a) CTAB; (b) NaLS.

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