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Effect of an Anionic Surfactant on the Kinetics of Base Catalysed Iodination of Acetophenones

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Kinetics of iodination of acetophenone by molecular iodine have been studied in varying composition of methanol-water mixture at different acidic pH maintained by acetic acid and sodium acetate buffer within a temperature range of 25–40°C in presence of sodium lauryl sulphate (NaLS) of different concentrations. The product of the reaction has been analysed. The thermodynamic quantities for the reaction have been computed and discussed.

INTRODUCTION

Acid and base catalysed halogenation of acetophenones have been reported by many workers.[1-3] Sundaram *et al.*[4] and Akhtar with his co-worker[5] have studied the kinetics of iodination of acetophenones catalysed by base. From literature survey it is ascertained that halogenation of some aromatic substrates[6] in the nucleus in presence of anionic surfactant sodium lauryl sulphate (NaLS) has been attempted but not much work seems to have been done on the iodination of acetophenones in the side chain using molecular iodine in presence of surfactant.

EXPERIMENTAL

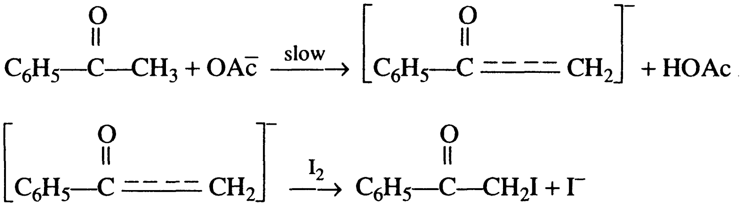
Materials: Sodium lauryl sulphate (BDH, England) was purified as described in the literature.[7] Other chemicals used are acetophenone, 4-nitroacetophenone, methanol (AR), iodine, sodium acetate, glacial acetic acid (AR) and sodium thiosulphate. Acetophenone was redistilled and iodine was resublimed before use. The remaining chemicals were of reagent grade and used as such. Methanol solution in double distilled water was used for the required solvent composition. The buffers were prepared by standard method.

Kinetics: 10 Ml of ketone solution of appropriate concentration in pure methanol, 25 ml of buffer solution in aqueous methanol with required volume of double distilled water taken in a dark coloured stoppered bottle and aqueous iodine solution of required concentration in another dark coloured bottle were preheated in a thermostatic bath in order to attain the desired temperature. Methanolic sodium lauryl sulphate (NaLS) solution of appropriate concentration and volume was taken in the reaction vessel replacing part or whole of distilled water when required. Then 10 ml of the iodine solution was transferred into the reaction vessel. It was shaken gently. The total volume of reaction mixture is always adjusted to be 50 ml. The pseudo first order condition is maintained with respect to ketone and iodine concentrations. The reaction was followed by quenching 5 ml of the reaction mixture in a conical flask containing ice. The unreacted iodine was estimated titrimetrically against standard sodium thiosulphate solution using starch as indicator in presence of carbon tetrachloride. The rate constant was computed graphically from the plot of log (a–x) against time using the expression $k_1 = \frac{2.303}{t} \times \log \frac{a}{(a-x)}$ where 'a' and (a–x) are concentrations of ketone at initial stage and after time 't'. All the rate constants are reported with standard deviations and in all cases the correlation co-efficient was found to be ≈0.99.

Product: The product of the reaction in presence of NaLS under the kinetic condition with acetophenone was isolated from the reaction mixture by extracting with ether and purified. It was characterised and found to be α-iodoacetophenone.

RESULTS AND DISCUSSION

The effect of anionic surfactant on the rate of iodination of acetophenone at different pH, solvent compositions and temperatures has been examined. In the case of *p*-nitroacetophenone iodination has been studied in varying concentration of NaLS in 50 : 50 v/v methanol-water at pH 5 and 35°C. The results are given in Tables 1–3. The reaction of acetophenone and substituted acetophenones with iodine is an electrophilic bimolecular substitution reaction. These reactions are catalysed by base and the mechanism can be represented as follows:



Step 1: $$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + O\bar{A}c \xrightarrow{\text{slow}} \left[C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}\text{-----}CH_2\right]^- + HOAc$$

Step 2: $$\left[C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}\text{-----}CH_2\right]^- \xrightarrow{I_2} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2I + I^-$$

The formation of carbanion by the attack of the base is a slower step than the step-2 and is therefore the rate determining step. Hence the rate of reaction depends on the concentrations of ketone and base but independent of that of iodine.[2] The steps of the mechanism is further supported from the product of this reaction.

Effect of anionic surfactant

It is well known that surfactants form aggregates called micelles in aqueous[8] and aquo-organic[9] media beyond certain concentration. The concentration at which such aggregation starts is called critical micelle concentration (CMC). In case of aquo-organic medium the CMC is higher than aqueous medium and also no aggregation is observed beyond certain proportion of organic solvent in the mixture.[10] Rate acceleration or inhibition of organic reaction in micellar solution arises due to uneven distribution of substrates in the bulk and micellar phase. These rate effects can be explained by considering the electrostatic and hydrophobic interactions between the substrate and surfactant aggregates.[11] In the present study the solvent composition of methanol-water has been maintained at

40 : 60, 45 : 55 and 50 : 50 v/v in the reaction mixture depending on the solubility of the substrate. Out of these three compositions micellar aggregates of NaLS is formed in 40 : 60 methanol-water (v/v) in the temperature range and at its concentrations studied. Panda *et al.*[9b] have reported CMC of NaLS at varying composition of methanol-water. In 40 : 60 ratio the CMC is 13.8×10^{-3}M at 25°C. According to them no aggregation was observed at and above 45 : 55 composition. Similar results have been published by Parfitt and co-workers[10] earlier. The rate constant (k_1) for the iodination reaction in presence of increasing concentration of NaLS was found to decrease (Tables 1–3) at different pH, solvent compositions and temperatures. In 40 : 60 v/v methanol-water micellar effect must have been experienced by the reactants. In other two compositions NaLS might have behaved as an electrolyte and exhibited negative salt effect in affecting the relative free energies of reactants and transition state.

TABLE 1
RATE CONSTANTS FOR IODINATION OF ACETOPHENONE AT DIFFERENT pH WITH THE VARIATION OF [NaLS] AT 25 ± 0.1°C IN METHANOL-WATER 50 : 50 v/v. [Acetophenone] = 0.25M, [Iodine] = 0.25M

(NaLS) in M	0.00	0.01	0.02 $k_1 \times 10^6$ sec^{-1}	0.03	0.04
pH					
4	7.68 ± 0.002	5.76 ± 0.001	4.60 ± 0.001	3.10 ± 0.001	1.50 ± 0.003
4.4	9.20 ± 0.002	6.70 ± 0.001	5.25 ± 0.001	—	2.00 ± 0.001
5	10.56 ± 0.002	7.00 ± 0.001	6.40 ± 0.001	5.5 ± 0.001	3.80 ± 0.001

The cause of rate retardation is the solubilization of acetophenone in the ionic micelle of NaLS due to the hydrophobic interaction and non-availability of the acetate ion (base) in the close proximity of solubilised acetophenone due to coulombic repulsion in 40 : 60 (v/v) methanol-water medium in which NaLS forms anionic micellar aggregates. Thus effective [acetophenone] decreases progressively in the bulk phase with increasing [NaLS] resulting in a decrease in the rate. Plots of k_1 vs. [NaLS] at different temperatures in this solvent composition are all curves. In other two solvent mixtures although micellar aggregate formation has been denied[9b] still considerable rate retardation was observed with increasing concentration of NaLS. Similar results have been obtained in case of *p*-nitroacetophenone in 50 : 50 v/v methanol-water mixture. Probably the long alkyl chain of the surfactant has certain contribution towards this effect.[12] The effect of premicellar dimers, trimers and smaller aggregates[13] on the reaction can not be ruled out. This decrease in rate cannot be simply due to negative salt effect.

Dependence of rate on [acetate ion]

The rates of iodination of acetophenone in acetic acid-acetate buffer of different pH in absence and presence of varying concentration of NaLS at 25°C have been determined (Table 1). It is observed that the reaction is accelerated with increase in pH as rate depends on [acetate ion] which is higher at higher pH values. The plots of log k_1 *vs.* log [acetate ion] are linear.

Effect of solvent composition on the reaction

The rate constants for this reaction are found to decrease with increasing methanol percentage in absence and presence of increasing concentration of NaLS (Table 2). The increase of methanol percentage in aquo-methanol mixture results in the decrease of its dielectric constant. Hence rate of iodination increases with increasing dielectric constant or polarity of the medium solvating the polar transition state. In an ion neutral molecule reaction the rate will be greater in a medium of lower dielectric constant as per Ingold rule[14] . The results of the present study contradicts this rule. Similar reverse findings have been reported by other workers[15]. The plots of log k_1 *vs.* $\frac{1}{D}$ (D = dielectric constant) are linear with negative slopes. This indicates that the reactant is more solvated than the activated complex[16].

TABLE 2

RATE CONSTANTS FOR IODINATION OF ACETOPHENONE AND *p*-NITRO-ACETOPHENONE IN VARYING CONCENTRATION OF NaLS AT pH 5 AND TEMPERATURE 35 ± 0.1°C IN VARYING AND FIXED SOLVENT COMPOSITION RESPECTIVELY.

[Acetophenone] = 0.25M, [Iodine] = 0.25M

[NaLS] in M	0.00	0.01	0.02	0.03	0.04	0.05
			$k_1 \times 10^6$ sec^{-1}			
Methanol: water (v/v)						
40 : 60	13.90 ± 0.003	11.50 ± 0.003	9.70 ± 0.002	8.10 ± 0.002	—	—
45 : 55	12.70 ± 0.003	10.75 ± 0.002	8.90 ± 0.002	6.70 ± 0.001	—	—
50 : 50	11.26 ± 0.002	9.20 ± 0.002	8.30 ± 0.002	5.70 ± 0.002	—	—
[*p*-Nitroacetophenone] = 0.05M,		[Iodine] = 0.005M				
50 : 50	20.10 ± 0.004	17.20 ± 0.003	14.50 ± 0.004	12.70 ± 0.003	11.90 ± 0.002	10.00 ± 0.01

Temperature effect and activation parameters

The rate of reaction has increased with rise in temperature from 30 to 40°C in absence and presence of varying concentration of NaLS at pH 5 in 40 : 60 v/v methanol-water mixture (Table 3). The activation and thermodynamic parameters have been computed from the respective Arrhenius plot and other related equations. The results are summarised in Table 3. The standard deviations have been indicated in E_a values and other parameters are calculated using the E_a values. In presence of 0.01M NaLS the activation energy, enthalpy and entropy have decreased but these parameters increased gradually at higher concentration of NaLS. The negative values of entropy of activation suggest that the transition state of the reaction is much more rigid than reactants in the ground state. The free energy of activation values are almost identical.

TABLE 3

RATE CONSTANTS FOR THE IODINATION OF ACETOPHENONE AT pH 5 IN 40 : 60 v/v METHANOL-WATER AT DIFFERENT TEMPERATURES AND ACTIVATIONS PARAMETERS*.

[Acetophenone] = 0.25M, [Iodine] = 0.025M

[NaLS] in M	$k_1 \times 10^6$ sec^{-1}			E_a in kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
	30 ± 0.1°C	35 ± 0.1°C	40 ± 0.1°C				
0.00	13.00 ± 0.004	13.90 ± 0.003	15.30 ± 0.003	13.78 ± 0.003	11.26 ± 0.003	104.92 ± 0.10	43.05 ± 0.06
0.01	11.00 ± 0.003	11.50 ± 0.003	12.28 ± 0.002	9.19 ± 0.02	6.67 ± 0.02	120.64 ± 0.04	43.23 ± 0.03
0.02	8.10 ± 0.002	9.70 ± 0.002	10.97 ± 0.002	16.75 ± 0.05	14.23 ± 0.05	96.53 ± 0.15	43.48 ± 0.09
0.03	7.10 ± 0.002	8.10 ± 0.002	8.90 ± 0.002	17.80 ± 0.04	15.28 ± 0.04	93.69 ± 0.11	43.67 ± 0.07

*$\Delta H^{\#}$, $-\Delta S^{\#}$, $\Delta G^{\#}$ values in Table 3 are at 30 ± 0.1°C.

Effect of *p*-nitro substituents

The rate of iodination of *p*-nitro acetophenone in varying concentration of NaLS (0.01 to 0.05M) at pH and 35°C in 50 : 50 MeOH-water has been measured (Table 2). It is seen that the pseudo first order rate constants are high in comparison to acetophenone under almost identical conditions. This is due to the electron withdrawing nature of the nitro group. Such substrituents in the phenyl nucleus of the acetophenones will increase the magnitude of the positive charge on the carbon atom of the carbonyl group and hence the reaction rate by facilitating deprotonation at the $-CH_3$ group. The rate of retardation has been observed with increasing [NaLS]. A plot of k_1 *vs.* [NaLS] has resulted a curve in this case, although micellar aggregation does not take place with this solvent composition.

In the present study retardation of iodination of acetophenone was observed in micellar and premicellar aggregates of NaLS. On increasing concentration of acetate ion and increasing dielectric constant of the medium the iodination rates have increased. Presence of electron withdrawing group at *para* position of the ring has produced expected kinetic result.

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