Kinetics of Phenylhydrazine-Glucose Reaction in Anionic and Cationic Surfactant Media

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Osazone formation by glucose has been shown to occur at room temperature in the presence of surfactants. The kinetics of this reaction reveal that the rate is increased by both anionic and cationic surfactants at premicellar concentrations whereas it is retarded at postmicellar concentrations. Also, in the presence of surfactants, the reaction depends on the first order on phenylhydrazine but is zero order with respect to glucose. A mechanism involving adsorption of phenylhydrazine on surfactant as a slow step followed by a fast attack by glucose is proposed.

INTRODUCTION

The reaction between phenylhydrazine and glucose producing glucosazone is a well-known reaction; however, this reaction occurs only at elevated temperatures requiring heating the reaction mixture to 70–80°C on a water bath. Our preliminary investigations on this reaction proved that it occurred easily and quantitatively at room temperature itself in the presence of a surfactant[1]. A similar effect of surfactant to catalyse the MnO_4^-—$H_2C_2O_4$ reaction at room temperature has also been noted earlier[2]. Consequently we have undertaken a detailed kinetic study of the title reaction in surfactant media and the results of this study are reported in this paper.

EXPERIMENTAL

Pure samples of phenylhydrazine (SDS-AR) and glucose (Qualigen-AR), sodium lauryl sulphate (BDH) and cetyl (trimethyl) ammonium bromide (Loba Chemie) are used. Solutions of phenylhydrazine were prepared freshly in pure acetic acid and distilled water respectively. Appropriate volumes of these solutions were mixed for reactions so that 60% aq. acetic acid is maintained in the reaction conditions. Kinetics of the reactions were followed spectrophotometerically using a UV-spectrophotometer (Chemito 2600) at 460 nm, which is the characteristic wavelength of the product osazone. The product obtained in this reaction has been identified to be glucosazone by matching its melting point and UV-visible spectral characteristics with those of the osazone product prepared by the traditional heating procedure reported in the textbooks of organic chemistry. This product is identical with the osazone obtained by the traditional heating method.

RESULTS AND DISCUSSION

Effect of [phenylhydrazine] on the rate: The kinetics of the reaction have been followed at different concentrations of phenylhydrazine in presence of the anionic surfactant—sodium laurylsulphate (NaLS) and the cationic surfactant—cetyl (trimethyl) ammonium bromide (CTAB) in 60% aqueous acetic acid. From the results obtained (Table-1) and from the slope of the plot of log k_1 against log [phenylhydrazine], it is found that the order on [phenylhydrazine] is unity.

TABLE-1

VARIATION OF [PHENYLHYDRAZINE] AT [GLUCOSE] = 0.01 M IN 60% aq. HOAc AT 60°C

[Phenylhydrazine] (M)	$k_1 \times 10^5 \; s^{-1}$	
	[NaLS] = 1.0×10^{-4} M	[CTAB] = 1.0×10^{-5} M
0.03	2.35	4.05
0.05	3.85	6.58
0.08	6.15	11.12
0.10	7.73	13.40

Effect of [glucose] on the rate: The reaction was conducted by varying the [glucose] keeping the other experimental parameters invariant in presence of a fixed [NaLS] and [CTAB] in 60% aq. acetic acid. The k_1 values thus obtained (Table-2) were found to be constant. This suggests that the reaction is zero order in [glucose].

TABLE-2

VARIATION OF [GLUCOSE] AT [PHENYLHYDRAZINE] = 0.05 M IN 60% aq. HOAc AT 30°C

[Glucose] (M)	$k_1 \times 10^5 \; s^{-1}$	
	[NaLS] = 1.0×10^{-4} M	[CTAB] = 1.0×10^{-5} M
0.005	3.86	6.51
0.008	3.83	6.50
0.010	3.85	6.58
0.015	3.89	6.52

Effect of [surfactant] on the rate: In the absence of any surfactant, the reaction is not even initiated at room temperature. However, the addition of a catalytic quantity (10^{-5} M) of sodium lauryl sulphate (NaLS), an anionic surfactant promotes the reaction. On increasing [NaLS], the k_1 values increase up to 1.0×10^{-4} M; subsequent increase in [NaLS] decreases the k_1 value (Fig. 1) and when [NaLS] exceeds 0.01 M, no noticeable reaction occurs.

A similar trend in k_1 values was observed when the reactions were conducted with cationic surfactant, cetyl (trimethyl) ammonium bromide (CTAB). With this
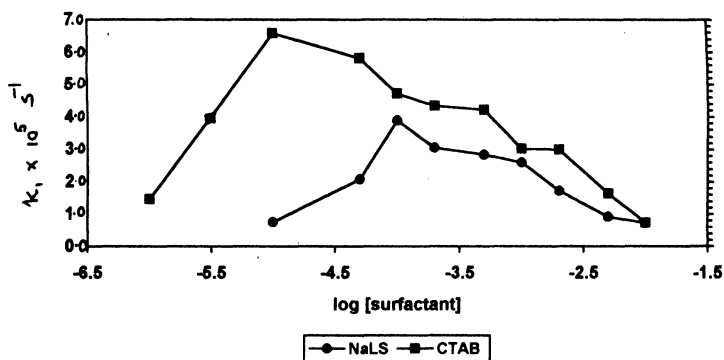
Fig. 1.　Effect of [Surfactant] on Rate

surfactant, as the [CTAB] is increased from 1.0×10^{-6} M, the rate increases and reaches a maximum at [CTAB] = 1.0×10^{-5} M. Further increase in [CTAB] inhibits the reaction leading to lower k_1 values and no noticeable reaction occurs when the [CTAB] is greater than 1.0×10^{-2} M, on observation analogous to that with the anionic surfactant (NaLS).

## Mechanism

The essential features of the kinetic data are:

(i) the order in [phenylhydrazine] is unity and that in [glucose] is zero.

(ii) the reaction is catalysed by both the anionic and cationic surfactants used at lower concentrations but inhibited at higher concentrations.

Phenylhydrazine, being less soluble in water, is more likely to be solvated by acetic acid; however, glucose will be solvated by water. The added surfactant may alter the rate of the reaction[3, 4] by

(i) influencing the dissociation constants of the reactants and hence the reactive species generated,

(ii) altering the redox potential of the system,

(iii) providing a thermodynamically favourable micro-micellar reaction environment, or

(iv) simply altering the properties of the reaction medium

Our observation that the anionic and the cationic surfactants behave more or less identically rules out the first two factors being responsible for the results observed in this study.

The observed order dependence, coupled with the fact that the reaction does not occur in the absence of surfactants, suggests the adsorption of phenylhydrazine (PH) on surfactant (S) molecules in a slow step followed by this surfactant-adsorbed phenylhydrazine (PH—S) reacting with glucose in a fast step as shown below, being the preferred sequence of reaction:

$$PH + S \overset{slow}{\rightleftharpoons} PH—S$$

$$PH—S + Glucose \overset{fast}{\longrightarrow} product$$
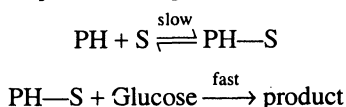
However, at higher concentrations, the surfactant would aggregate to form micelles. Consequently the less-water-soluble phenylhydrazine molecules will be drawn into the inner non-polar core and encased in the micelles while glucose will be left out in the bulk solvent. This renders the effective collisions of the two reactant molecules less probable, thus resulting in a decrease in rate with increase in [surfactant], and ultimately at higher micellar concentrations (> 0.01 M) the reaction practically ceases.

Thus, the unique characteristics of surfactants to provide conducive environment for reactions to occur at milder conditions and the possibility of controlling the reaction rate by adjusting the micellar concentrations are exemplified in this work.

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