Micellar effect on methylaminolysis of O-(2,4-dinitrophenyl)cyclohexanone oxime

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The cleavage of C-O bond of O-(2,4-dinitrophenyl)cyclohexanone oxime by methylamine in aqueous methanol [70:30 (v/v)] has been found to be acid-catalysed. Effect of cationic micelles supports the view that the protonation of oxygen of the leaving group is an important step in determining overall rate of the reaction.

Recently from this laboratory, Malik and coworkers reported that O-(2,4-dinitrophenyl)cyclohexanone oxime (DNPCHOX) when treated with nucleophile underwent substitution at the nitrogen atom of the oxime moiety. Later we found that with OH as a nucleophile, the site of attack was the aromatic carbon attached to the oxime oxygen and cleavage of the C-O bond occurred. These investigations were further extended to study the effect of nature of amine on the aminolysis of various oxime ethers both in 1:1 aqueous acetonitrile and other non-aqueous media. We report herein the effect of cationic micelles on the methylaminolysis of DNPCHOX in 70:30 (v/v) aqueous methanol.

Experimental

The substrate was prepared by the method described elsewhere. All chemicals and solvents were of AR grade and used as such. Kinetics of the reactions were followed spectrophotometrically at 360 nm and 35 ± 0.1°C, under pseudo-first order conditions at a constant ionic strength of 0.1 mol dm⁻³ (NaClO₄) using an UNICAM SP 500 spectrophotometer. (The reaction product N-methyl-2,4-dinitroaniline absorbs at 360 nm).

To study the pH effect, the amine to salt ratio of buffer solution was varied, keeping [free amine] fixed. The rate constants were calculated by a least square fit of the plot of log (Aₓ₋₁ - Aₓ₋ₐ)/(Aₓ₋₁ - Aₓ₋ₐ) versus time, where Aₓ₋₁, Aₓ₋ₐ, Aₓ are absorbances of the reaction mixture at infinity, zero and time t, respectively. All rate calculations were done with the help of a DEC-2050 computer.

Results and discussion

Methylamine reacts with DNPCHOX to give N-methyl-2,4-dinitroaniline, the formation of which was confirmed by spectral data and TLC. The reaction was found to be first order each in [substrate] and [methylamine]. At fixed pH, temperature and ionic strength, pseudo-first order rate constant increased linearly with [amine] indicating the absence of general base or acid catalysis. The reaction proceeds through the mechanism already given. That the protonation of oxime oxygen occurs prior to expulsion of oxime moiety is indicated by rate enhancement with gradual decrease in pH at fixed [free amine] (see Fig.1). Second order rate constant and catalytic rate coefficient were found from the linear portion of the plot in Fig.1 and the values are 8.7 × 10⁻³ dm³ mol⁻¹ s⁻¹ and 6.3 × 10⁶ dm⁶ mol⁻² s⁻¹, respectively.

Effect of micelles

Reaction was carried out in the presence of cationic surfactant, cetyltrimethylammonium bromide (CTMAB). The critical micelle concentration (cmc) of the surfactant in 70:30 (v/v) aqueous methanol was determined to be 5.0 × 10⁻⁴ mol dm⁻³. It is seen from the Fig.2 that the reaction rate decreased in the presence of CTMAB. This may be due to the fact that the micelles of the surfactant are able to solubilise the hydrophobic substrate. This is evident from the fact that DNPCHOX which is insoluble in water dissolves in dilute aqueous solution of CTMAB above cmc. Similarly it was experimentally shown that methylamine exhibited an absorption maximum at 208
nm which shifted to 214 nm in the presence of CTMAB and the absorbance was also considerably reduced. This shift in absorption maximum of methylamine indicates incorporation of methylamine by the micelles. Thus in the presence of micelles, DNPCHOX and methylamine are partitioned between the micellar and the bulk phase. As [substrate] and [methylamine] are increased in the micellar phase which is in close contact, the rate is expected to increase if the only rate-determining step is the attack of the amine on the substrate. However, the observed decrease in rate rules this out.

The positively charged micelles repel [H\(^+\)] and consequently pH in the Stern layer of the micelle is higher than that in the bulk. Thus the reaction occurring in the micellar phase would be retarded at higher pH. This supports the concept that the protonation of the oxygen of the leaving group is an important step in determining overall rate of the reaction. The initial small decrease (Fig. 2, portion AB) in the rate is due to premicellar association\(^{10,11}\) and thereafter the sharp decrease is due to the micelles (see Fig. 2). The concentration above which sharp decrease in rate occurs is the cmc and is found to be \(4 \times 10^{-4}\) mol dm\(^{-3}\) from the plot. This value is slightly less than the cmc of CTMAB \((5 \times 10^{-4}\) mol dm\(^{-3}\)) determined in 70:30 (v/v) aqueous methanol due to solubilization of the substrate\(^{12}\). The portion, CD of the plot in Fig. 2 which shows practically negligible effect on the rate with increase in [CTMAB] may correspond to complete transfer of the substrate in the micelle and thus further increase in [CTMAB] does not cause any decrease in the rate.

References