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Kinetic Studies and Solvent Effect on the Pyrrolidinolysis of Some Nitro Activated O-aryl Oximes

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The effect of two solvent parameters, hydrogen bond acceptor ability and the dielectric constant, on the mechanistic pathway of the pyrrolidinolysis of nitro-activated O-aryl oximes has been kinetically investigated.

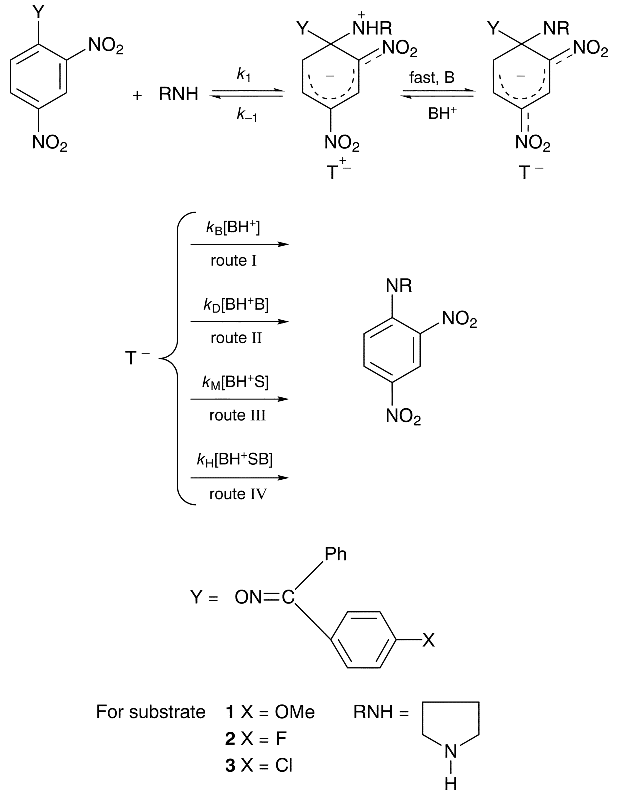
The third order dependence on amine for many aminolysis reactions in apolar solvents can be explained by involving the concept of electrophilic catalysis by homoconjugates[3,7] BH^+ (where $B =$ nucleophile). Solvent parameters such as the dielectric constant (D) and the hydrogen bond acceptor ability[8] (β) are expected to affect the stability of the hydrogen bonded homoconjugates BH^+B and, thus, may affect the course of the reaction. A study of the effect of these two parameters on the reaction rate may, thus, provide evidence in support of a particular reaction mechanism. Therefore, a comparative study of the pyrrolidinolysis of three nitro-activated O-aryl oximes, *O*-(2,4-dinitrophenyl)-*p*-methoxybenzophenone oxime (**1**), *O*-(2,4-dinitrophenyl)-*p*-fluorobenzophenone oxime (**2**) and *O*-(2,4-dinitrophenyl)-*p*-chlorobenzophenone oxime (**3**), in benzene, chlorobenzene and dioxane was taken up and the results are reported here.

The three substrates prepared[9–12] were characterized by elemental analysis, UV-VIS, IR and ^{1}H NMR spectroscopy (100 MHz). Their reactions with pyrrolidine were carried out under pseudo-first order conditions at different temperatures in the thermostatted multicell compartment of a Shimadzu 160A UV-VIS spectrophotometer and were monitored by measuring the absorbance at $\lambda_{\max}$ (373 nm) of the aminolysis product. The rates for different substrates follow the order **3** > **2** > **1** in the three solvents and can be explained[10] in terms of the lability of the leaving group. Plots of $k_A[B]^{-1}$ *versus* [B] ($k_A =$ second order rate constant) are linear for all the substrates in benzene, chlorobenzene and dioxane, indicating similar behaviour in terms of the third order dependence on amine. These results can be explained by adopting Scheme 1 wherein the concept of the electrophilic catalysis[3,7] by conjugate, homoconjugate and heteroconjugate acids has been invoked. The reactions in benzene ($\beta = 0.10$, $D = 2.2$) and chlorobenzene ($\beta = 0.07$, $D = 6.0$), which have almost similar hydrogen-bonding acceptor abilities but different dielectric constants, are assumed to proceed through routes I and II and analysis of data shows that, compared with benzene, the relative contribution of route I to the overall rate (k_A) in chlorobenzene is increased and that of route II decreased. This is apparently owing to the lower stability of the hydrogen bonded BH^+B species in chlorobenzene which has a higher dielectric constant. Thus, the results indicate that with increasing dielectric constant the reaction moves from third order dependence (BH^+B route) to second order (BH^+ route) in amine, and in solvents of higher polarity the second order dependence only is observed. Such behaviour has already been reported by us for dimethyl sulfoxide, acetonitrile and dimethylformamide.[14]

The pyrrolidinolysis of the substrates in benzene and in dioxane ($\beta = 0.37$, $D = 2.2$), solvents with the same dielectric constant but different hydrogen bond acceptor abilities, also, surprisingly, shows similar behaviour, *i.e.* in both solvents a third order dependence on amine is observed. It was expected that the formation of BH^+B would be prevented in dioxane, and instead BH^+S ($S =$ dioxane) would form. This is a reasonable assumption in view of the good hydrogen bond acceptor ability of dioxane and its much larger concentration compared with the nucleophile. Thus, catalysis by BH^+S should give rise to a second order dependence on amine. Contrary to this, a third order dependence on amine in dioxane too indicates a catalytic step involving two amine molecules. This could be accounted for on the basis of two hydrogen bond acceptor sites on dioxane molecule. As such, the heteroconjugate BH^+S is still left with one hydrogen bond acceptor site to which another molecule of the nucleophile can be hydrogen bonded, as per the equilibria

$$BH^+S + B \rightleftharpoons BH^+SB$$

The third order dependence can be explained as a result of the reaction proceeding through a route involving catalysis by a mixed heteroconjugate, BH^+SB. Thus, in dioxane the pyrrolidinolysis proceeds through routes I, III and IV, and the results obtained conform to the kinetic equation thereby derived.



Scheme 1

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In addition, analysis of the data indicates that the rate of the route catalysed by BH^+ increases and that of the route catalysed by BH^+B/BH^+SB decreases with a rise in temperature. The energy and entropy of activation have been determined for separate routes and the values obtained support the mechanism adopted. Thus, it is reasonable to conclude that the mechanistic pathway for aminolysis reactions depends both on the dielectric constant and the hydrogen bond acceptor ability of the medium.

Techniques used: Elemental analysis, TLC, UV-VIS, IR, ^{1}H NMR

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Fig. 1: Plots of $k_A[B]^{-1}$ *versus* [pyrrolidine] for the pyrrolidinolysis reactions of **1**–**3** in benzene and in chlorobenzene at 20 °C

Fig. 2: Plots of $k_A[B]^{-1}$ *versus* [pyrrolidine] for the pyrrolidinolysis reactions of **1**–**3** in benzene and in dioxane at 20 °C

Table 1: Third and fourth order catalytic rate coefficients for the pyrrolidinolysis of **1**–**3** in different solvents at three different temperatures

Table 2: Energy and entropy of activation for separate routes for the pyrrolidinolysis of **1**–**3** in different solvents

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