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Kinetics and Mechanism of Dehydrochlorination of *N*-Aryl 2-Oxo-2-phenylaminoethanehydrazonoyl Chlorides and their Mass Spectra

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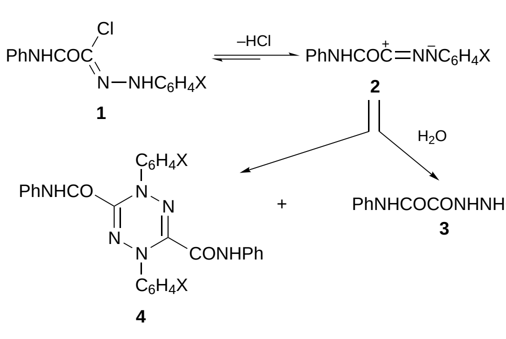
The dehydrochlorination mechanism of the title compounds in solution and inside a mass spectrometer is studied.

A number of studies on the chemistry of *N*-aryl 2-oxo-2-phenylaminoethanehydrazonoyl chlorides **1** have been reported in the literature,[1,2] However, the kinetics of the base catalysed dehydrochlorination of such compounds have not yet been reported. We now report the kinetics and mechanism of such a process. In addition, the mass spectra of **1** were also studied to compare their unimolecular reactions in the mass spectrometer to those that would occur under normal solution conditions.

A series of compounds **1a–i** were prepared by reported methods.[3] The structures of the new derivatives **1a** and **1h** were substantiated by both elemental and spectral (IR, ^{1}H NMR and mass) analyses. Treatment of **1** with triethylamine in 1,4-dioxane–water (4:1 v/v) at 25 °C gave a mixture of the corresponding oxanilic hydrazide **3** and 1,4-diaryl-1,2,4,5-tetrazine **4**. Such products are undoubtedly formed *via* the addition of water to the nitrilium imide **2** and by a head-to-tail dimerization of **2** which is generated *in situ* by the action of triethylamine on **1** (Scheme 1). The kinetics of the formation of **2** from **1** were carried out under pseudo-first order conditions by keeping an excess ($\times 10$ or greater) of triethylamine over **1** in 1,4-dioxane–water (4:1 v/v) at 25 ± 0.1 °C with an ionic strength of 0.1. The reactions were followed potentiometrically up to 90% reaction extent by monitoring the increase in the chloride ion concentration using an ion selective electrode. The ionic strength was maintained at 0.1 in all the kinetic runs by the addition of the appropriate volume of sodium nitrate solution (5 M) in the same solvent system. The pseudo-first-order rate constant, k_0, was computed from the linear ($r^2 > 0.990$) least squares plot of $\log (C_\infty - C_t)$ *vs.* time where C_∞ and C_t are the concentrations of the chloride liberated at infinite time and time t, respectively. The second-order rate constant, k_2, was determined from the relation $k_2 = k_0/[\mathrm{Et_3N}]$. In all cases, the plots of k_0 *vs.* [Et$_3$N] have zero intercepts indicating that the uncatalysed reaction is negligible under the reaction conditions employed.



a X = 4-MeO **f** X = 4-EtOCO
b X = 4-Me **g** X = 3-NO$_2$
c X = H **h** X = MeCO
d X = 4-Cl **i** X = 4-NO$_2$
e X = 3-Cl

Scheme 1

The second-order rate constant, k_2, gave an excellent correlation with the substituent constant σ_x^-. The equation of the regression line is:

$$\log k_2 = 0.37\sigma_x^- - 0.77;$$

where $r = 0.940$ and $s = \pm 0.09$. A mechanism compatible with the small ρ_2 value (0.37) is presented in Scheme 2. According to this suggested mechanism, it can be shown that $k_2 = K_a k_1$ and in turn the overall reaction constant ρ_2 will be the algebraic sum of ρ_a and ρ_1. These two reaction constants are expected to have opposite algebraic signs, ρ_a being positive whereas ρ_1 being negative. Such opposite effects would thus lead to a small ρ_2. This conclusion was substantiated by measuring the acid dissociation constants, pK_a, of the related hydrazone series **5a–i** in 1,4-dioxane–water (4:1 v/v) at 25 ± 0.1 °C and ionic strength of 0.1. The choice of **5** was based on the similarity of the inductive effects of the CN and Cl groups (σ_I values of CN and Cl are 0.60 and 0.47, respectively).[5]

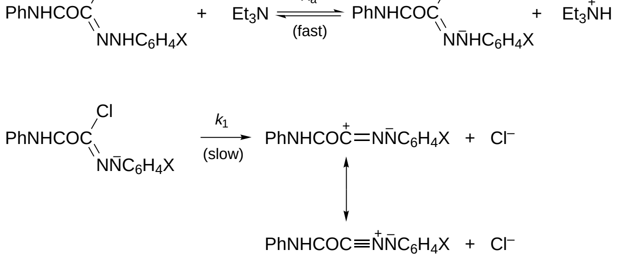
PhNHCOC(CN)=NNHC$_6$H$_4$X **5**   PhC(Br)=NNHC$_6$H$_4$X **6**

PhC(Cl)=NC$_6$H$_4$X **7**

The pK_a data of **5a–i** also showed an excellent correlation with σ_x. The equation of the regression line is:

$$\log K_a = 1.18\sigma_x^- - 0.87$$

where $r = 0.996$ and $s = \pm 0.01$. Substitution of the values of ρ_a (1.18) and ρ_2 (0.37) in the equation $\rho_2 = \rho_a + \rho_1$ gives a ρ_1 value of -0.81 which compares favourably with that (-0.63) reported for the heterolysis of the C—Br bond of *N*-aryl benzenecarbohydrazonoyl bromides **6** in the same solvent system and at the same temperature.[7] Furthermore, a comparison of the value of ρ_1 (-0.81) obtained in this work with that reported for the heterolysis of the C—Cl bond in the imidoyl chlorides **7** ($\rho_7 = -2.75$) indicates that the transmission factor $\pi' = (\rho_1/\rho_7)$ of the substituent effects for the trivalent anionic nitrogen bridge is 0.29. This small efficiency of anionic nitrogen to transmit substituent effects indicates that the changes in K_a are dominant in the studied reaction, that is the changes in k_2 ($= K_a k_1$) are mainly due to changes in K_a.



Scheme 2

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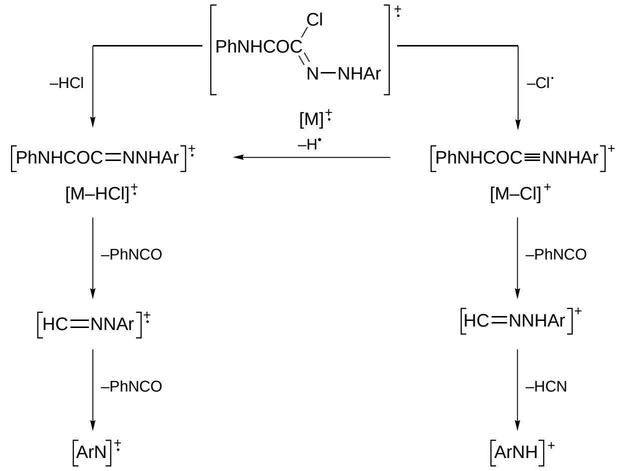

Scheme 3

The mass spectra show that the molecular ions of **1** seem to undergo fragmentation *via* the two possible routes outlined in Scheme 3. The data indicate that the ions $[M-Cl]^+$ are considerably less abundant than $[M-HCl]^+$ indicating that the formation of the latter is more favourable than the formation of the former azocarbocation. Furthermore, the data reveal that the abundance of the $[M-HCl]^+$, which formally corresponds to the nitrilium imide seems to depend on the nature of the substituent of the *N*-aryl of the hydrazone moiety which is increased by electron-withdrawing substituents.

Techniques used: Potentiometry, spectrophotometry, correlation analysis, mass spectrometry

References: 12

Fig. 1: Plots of k_2 for the base catalysed dehydrochlorination of **1a–i** and pk_as for the acid ionization of **5a–i** against the substituent constant σ_x

Table 1: Melting points and spectral data of the new compounds **1a**,**h**,**4c** and **5f**,**h**

Table 2: Second-order rate constantss, k_2, for dehydrochlorination of **1a–i** and acid dissociation constants, pK_a, of **5a–i** in 1,4-dioxane–water (4:1 v/v) at 25 °C and ionic strength of 0.1

Table 3: The principal peaks in the mass spectra of the hydrazonoyl chlorides **1a–i**

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