Identification of a Baker-type Mechanism in Additions to p-Nitrophenyl Isothiocyanate in Diethyl Ether Solution

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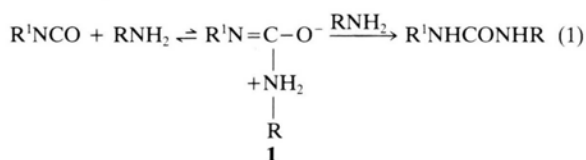King's College London, Strand,
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Kinetic evidence is presented which strongly suggests that in the diethyl ether solution the aminolysis of p-nitrophenyl isothiocyanate proceeds via a mechanism involving a 1:1-addition intermediate which undergoes catalyzed prototropic rearrangement to the product (Baker-type mechanism).

As a result of kinetic studies of the spontaneous alcoholysis and aminolysis of isocyanates in non-hydroxylic solvents, Baker and co-workers [1, 2] suggested a mechanism [shown for aminolysis in equation (1)] in which an addition intermediate, possibly **1**, undergoes catalyzed prototropic

$$R^1NCO + RNH_2 \rightleftarrows R^1N=C-O^- \xrightarrow{RNH_2} R^1NHCONHR \quad (1)$$

$$\begin{array}{c} | \\ +NH_2 \\ | \\ R \\ \mathbf{1} \end{array}$$

rearrangement. Subsequent work has shown that this type of mechanism is not, in fact, satisfactory for alcoholysis, and that a mechanism in which nucleophilic attack and proton transfer are concerted, and involve associated nucleophile, is likely [3, 4, 5]. Such a mechanism [equation (2)−(3)] also provides a better explanation of existing kinetic findings for aminolysis [3].

$$2 RNH_2 \rightleftharpoons (RNH_2)_2 \quad (2)$$

$$R^1NCO + (RNH_2)_2 \longrightarrow \begin{bmatrix} R^1-N=C=O \\ H \quad (N-H \\ H-N \quad /\ \\ | \quad H \quad R \\ R \end{bmatrix} \longrightarrow \begin{array}{c} R^1NHCONHR \\ + RNH_2 \end{array} \quad (3)$$
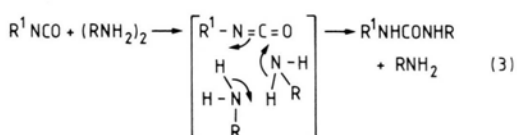
Amines also add spontaneously to isothiocyanates in non-hydroxylic solvents [6, 7] (to give thioureas)

and with a sufficient excess of amine the equilibrium position lies well to the right [equation (4)]. The mechanism of these

$$R^1NCS + RNH_2 \rightleftarrows R^1NHCSNHR \quad (4)$$

reactions has been little studied [6]. We have now examined kinetically the reactions of dibenzylamine and p-anisidine with p-nitrophenyl isothiocyanate (**2**) in diethyl ether solution, and have found evidence that suggests a Baker-type mechanism of addition.

Experimental

We used pseudo-first-order conditions ([**2**]$_{initial}$ = $5 \cdot 10^{-5}$ mol dm^{-3}; [amine] = ca. $10^{-3}-10^{-1}$ mol dm^{-3}) and normally followed the appearance of product spectroscopically (at ca. 310 nm) employing redistilled amines and ether dried with sodium and molecular sieves. **2** was a pure commercial sample (Aldrich). We found that the rate of loss of **2** (= rate of formation of thiourea) was always accurately first order over several half-lives, and the observed rate constants, k_{obs}, were reproducible to within ±5%. Reaction mixtures remained homogeneous throughout a run. In preparative-scale reactions the amines lead to high yields of the expected unsymmetrical thioureas (identified by NMR, and having the same UV spectra as obtained in the kinetic runs).

Results and Discussion

The effects on k_{obs} of changing the amine concentration are shown in Fig. 1: at the lower amine concentrations k_{obs} shows a greater than first-order dependence on [amine], but this order falls to close to unity at the higher values of [amine]. Unlike some systems [5] for the present systems (in which the pro-
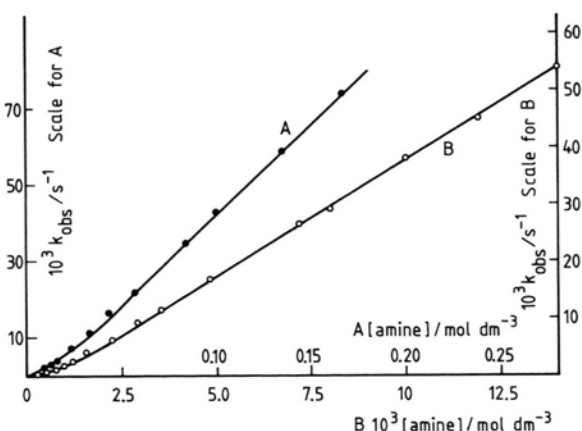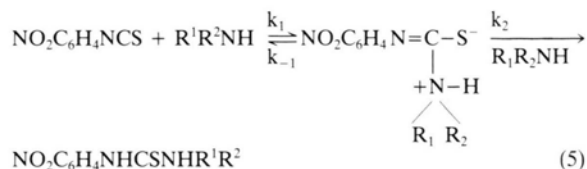

Fig. 1. A: p-Anisidine at 24.6 ± 0.1 °C; B: Dibenzylamine at 13.8 ± 0.1 °C.

portion of polymeric amine will be small [8]) it is difficult to explain this pattern of kinetic results other than by a Baker-type mechanism (eq. (5)) involving some (low concentration) intermediate whose catalysed conversion to the product by a second molecule of amine (k_2 step) becomes relatively fast at large values of [amine]. Thus the rate equation corresponding to (5) is eq. (6), which reduces to $k_{obs} = k_1[R^1R^2NH]$ when $k_2[R^1R^2NH] \gg k_{-1}$.

$$NO_2C_6H_4NCS + R^1R^2NH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2C_6H_4N=C-S^- \underset{R_1R_2NH}{\overset{k_2}{\longrightarrow}}$$
$$\underset{\overset{\mid}{+N-H}}{}$$
$$\underset{R_1 \quad R_2}{}$$

$$NO_2C_6H_4NHCSNHR^1R^2 \qquad\qquad (5)$$

$$k_{obs} = k_1k_2[R^1R^2NH]^2/(k_{-1}+k_2[R^1R^2NH]) \qquad (6)$$

The continuous curves in the Figure fit the experimental points satisfactorily; the curves were constructed from equation (6) using $k_1 = 4.16\,mol^{-1}dm^3s^{-1}$ and $k_2/k_{-1} = 1.04 \cdot 10^3 mol^{-1}dm^3$ for dibenzylamine, and $k_1 = 0.48\,mol^{-1}dm^3s^{-1}$ and $k_2/k_{-1} = 85.8\,mol^{-1}dm^3$ for anisidine. These parameters were obtained from plots of $[amine]^2/k_{obs}$ against [amine].

Invocation of Baker's mechanism for additions to isocyanates and isothiocyanates is often unsupported by evidence; where evidence has been provided it has, as noted above, so far proved open to an alternative and preferred interpretation [3, 4, 5, 7]. The present results seem less open to the alternative previously proposed. Perhaps the presence of the sulphur atom stabilizes the intermediate for isothiocyanates.

The few [7, 9] existing studies of spontaneous addition of amines to isothiocyanates in non-hydroxylic solvents used mostly second-order kinetic conditions, and suggest either a simple first- or second-order dependence on [amine]. These studies would not have been able easily to detect the gradual changes in reaction order we have now found.

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