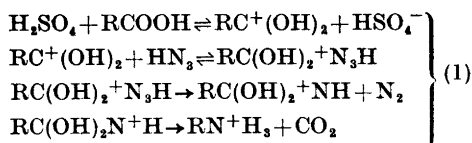# The Mechanism of the Homogeneous Schmidt Reaction

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It is usually assumed that the mechanism of the Schmidt reaction is the following [1]

$$H_2SO_4 + RCOOH \rightleftharpoons RC^+(OH)_2 + HSO_4^-$$
$$RC^+(OH)_2 + HN_3 \rightleftharpoons RC(OH)_2^+N_3H$$
$$RC(OH)_2^+N_3H \rightarrow RC(OH)_2^+NH + N_2$$
$$RC(OH)_2N^+H \rightarrow RN^+H_3 + CO_2$$
$$\qquad(1)$$

in which the rearrangement is occurring during the last two steps. Instead of $RC^+(OH)_2$ the reacting ion may be RC^+O. If the reaction is carried out homogeneously, for instance using concentrated sulfuric acid as a solvent, some implications of this mechanism can be tested quite easily. In concentrated sulfuric acid we have the equilibrium

$$HN_3 + H_2SO_4 \rightleftharpoons H_2N_3^+ + HSO_4^-$$
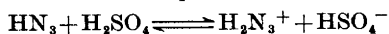
and since [2] pK_A for $H_2N_3^+$ is around -6.2, almost all hydrazoic acid is found as $H_2N_3^+$ in concentrated sulfuric acid. (% $H_2SO_4 > 90$, $-H_0 > 8$). Similarly, although most carboxyl and carbonyl compounds are extremely weak bases [3] (*i.e.* pK_A of the corresponding acid ~ -7.5) dissolved in sufficiently strong sulfuric acid, they will be ionized to a considerable extent.

Since it is usually assumed that the rate determining step in the reaction is the reaction between HN_3 and $RC^+(OH)_2$ one would assume that in sufficiently acidic solutions the reaction follows the ratelaw

$$-\frac{dC_{RCOOH}}{dt} = kC_{RCOOH}C_{HN_3} \qquad(2)$$

in which the measured second order rate constant is inversely proportional to h_0. Here C_X denotes the total (stoichiometric)

concentration of X and h_0 is related to Hammett's acidity function H_0 by [4]

$$H_0 = -\log h_0$$

h_0 is, therefore, roughly speaking an activity of H^+ and the reason for the above given dependence of the rate on the acidity is that in concentrated sulfuric acid solution we have

$$\left.\begin{array}{l} [H_2N_3^+] \sim C_{HN_3} \\[6pt] [RC^+(OH)_2] \sim C_{RCOOH} \\[6pt] [HN_3] \sim \dfrac{K_A^{(1)}C_{HN_3}}{h_0} \end{array}\right\} \qquad(3)$$

where $K_A^{(1)}$ is the dissociation constant for the acid $H_2N_3^+$.

More generally, if the mechanism given by eqn. (1) is correct, one would expect the measured second order rate constant k to equal

$$k = k_1 \frac{h_0}{(h_0 + K_A^{(1)})(h_0 + K_A^{(2)})} \qquad(4)$$

in which $K_A^{(2)}$ is the dissociation constant for $RC^+(OH)_2$ and k_1 is the "true" second order rate constant for the rate determining step in the mechanism given by eqn. (1). A consequence of this is that for $H_0 > \sqrt{K_A^{(1)}K_A^{(2)}}$, k is a decreasing function of $-H_0$ and for large positive values of $-H_0$ the dependence will be as the one given above.

We have measured the rate of the Schmidt reaction between benzoic acid and hydrazoic acid using the equipment described earlier.[5] The acids were dissolved in concentrated sulfuric acid ($90-98$ % H_2SO_4) in a sufficiently dilute solution so that H_0 did not change during the reaction. A correction was made for the change in H_0 due to the solution of RCOOH and HN₃ in the sulfuric acid, assuming that the change in H_0 which they cause is equal to that caused by the same number of moles of water.

We found that the second order rate constant depends on h_0 in the following way

$$k = \alpha + \beta h_0 \qquad(5)$$

in which at 25°C, $\alpha = 8.39 \times 10^{-3}$ l mol⁻¹ min⁻¹ and $\beta = 1.26 \times 10^{-11}$ l mol⁻² min⁻¹. Fig. 1 shows the results obtained at 25°C. Similar results have been obtained at 35°C and at

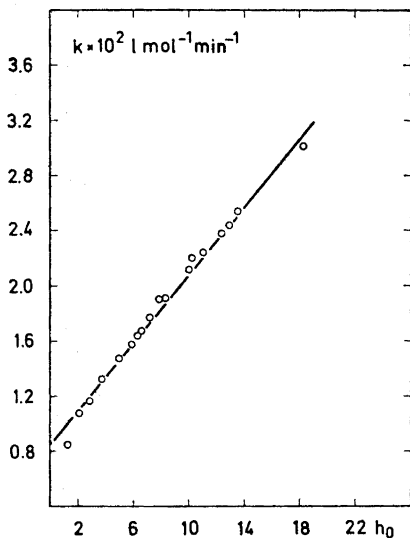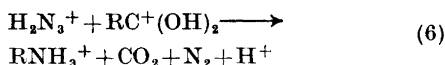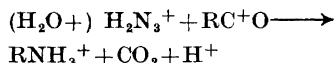*Fig. 1.* The observed second order rate constant at 25°C as function of h_0.

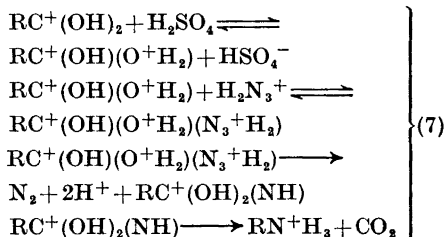40°C. Since both α and β are positive, k is an increasing function of h_0 and we can immediately rule out the notion that HN_3, the "most basic" acid involved, is reacting in its non-protonated form. Hence the rate determining step in the reaction, or the equilibrium immediately preceding it, must involve the species $H_2N_3^+$. Since it is necessary that the reacting carbon atom is present as a carbonium ion we have two possible reactions:

$$H_2N_3^+ + RC^+(OH)_2 \longrightarrow \tag{6}$$
$$RNH_3^+ + CO_2 + N_2 + H^+$$

and

$$(H_2O+) \ H_2N_3^+ + RC^+O \longrightarrow$$
$$RNH_3^+ + CO_2 + H^+$$

but we shall prefer to write the later reactions as

$$\left.\begin{array}{l}RC^+(OH)_2 + H_2SO_4 \rightleftharpoons \\ RC^+(OH)(O^+H_2) + HSO_4^- \\ RC^+(OH)(O^+H_2) + H_2N_3^+ \rightleftharpoons \\ RC^+(OH)(O^+H_2)(N_3^+H_2) \\ RC^+(OH)(O^+H_2)(N_3^+H_2) \longrightarrow \\ N_2 + 2H^+ + RC^+(OH)_2(NH) \\ RC^+(OH)_2(NH) \longrightarrow RN^+H_3 + CO_2\end{array}\right\} \tag{7}$$

In all cases H^+ means a proton species present in the solution as H_3O^+ or as $H_3SO_4^+$.

In the reaction given in eqn. (6) the actual concentrations of $H_2N_3^+$ and $RC^+(OH)_2$ are both virtually independent of h_0 and hence the measured second order rate constant is independent of h_0. This reaction therefore accounts for the term α in eqn. (5). In the reaction given by eqn. (7) the concentration of $RC^+(OH)(O^+H_2)$ is proportional to h_0 or strictly speaking to h_+, but at high sulfuric acid concentration these two acidity functions are proportional.[6] Since $H_3N_3^+$ is independent of h_0 this reaction contributes the term βh_0 in eqn. (5). If the very reactive molecule $RC^+(OH)(O^+H_2)$ should react with the very rare species HN_3 we would just get an extra contribution to the term α, since $|HN_3| \sim h_0^{-1}$.

The measurements presented here do not allow us to draw any conclusion as to the magnitude of rate constants and equilibrium constants, but they do allow us to suggest that in the homogeneous Schmidt reaction $H_2N_3^+$ plays a much greater role than so far assumed. For the non-homogeneous Schmidt reaction, which probably is of greater importance from the point of view of organic synthesis, no such statement can be made, obviously, since generally the reaction there takes place at an interphase.

1. See for instance: Newmann, M. S. and Gildenhorn, H. L. *J. Am. Chem. Soc.* **70** (1948) 317.
2. Bak, T. A. and Præstgaard, E. *Acta Chem. Scand.* **10** (1957) 901.
3. Hammett, L. P. *Physical Organic Chemistry*, McGraw, New York 1940, p. 271.
4. Hammett, L. P. and Deyrup, A. J. *J. Am. Chem. Soc.* **55** (1933) 1900; Hammett, L. P. *Physical Organic Chemistry*, New York 1940, p. 267.
5. (a) Birkhimer, E. A., Norup, B. and Bak, T. A. *Acta Chem. Scand.* **14** (1960) 1894; (b) Jensen, K. A., Burmester, S. and Bak, T. A. *Acta Chem. Scand.* **21** (1967) 2792.
6. Brand, J., Horning, W. and Thornley, M. B. *J. Chem. Soc.* **1952** 1374; Paul, M. and Long, F. A. *Chem. Rev.* **57** (1957) 1.