Comment on "Phenylureas. Part 1. Mechanism of the basic hydrolysis of phenylureas and Part 2. Mechanism of the acid hydrolysis of phenylureas" by R. Laudien and R. Mitzner, *J. Chem. Soc., Perkin Trans. 2*, 2001, 2226 and 2230

Stefano Salvestrini, Paola Di Cerbo and Sante Capasso *

Dipartimento di Scienze Ambientali, Seconda Università di Napoli, via Vivaldi 43,
81100 Caserta, Italy

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An elementary analysis of recently published experimental kinetic data evidences some aspects that should have been considered before proposing the kinetic mechanisms.

Two consecutive papers by the same authors on the hydrolysis of phenylureas have been recently published in this journal, 2001, Issue 11.[1,2] The two papers respectively report an investigation on the hydrolysis of about thirty phenylureas in acidic and basic media and postulate two reaction pathways one operating in acidic media and the other in basic media. According to the mechanism proposed for acidic media, there is first protonation of the substrate followed by a rate-determining attack by water, giving a tetrahedral intermediate. Decomposition of the intermediate gives an amine and a phenylcarbamic acid which decarboxylates to give aniline.[1] In basic media it is proposed that the hydrolysis of phenylureas occurs *via* an addition–elimination mechanism in which an intermediate hydroxide ion complex is formed.[2] Salient points for the mechanisms are that in basic media, from 0.005 to 0.9 mol l^{-1} NaOH, the rate constant is not directly proportional to the hydroxide concentration, but tends towards a limiting value at high hydroxide concentrations. In acidic media (from 0.001 to 0.9 mol l^{-1} H_2SO_4) the rate constant rises, again, to a limiting value with acid concentration, then decreases at higher acid concentrations due to reduction of water activity.

Reported separately in each of the above papers are the values of the kinetic constants for about thirty phenylureas, respectively recorded in 0.1 mol l^{-1} H_2SO_4) and 0.1 mol l^{-1} NaOH. The point that mainly drew our attention was that for every compound the rate constants had an identical value, within the experimental errors, both in acidic and basic media. The mean value of the ratios of the rate constants in acidic pH to the rate constant in basic pH at 80 °C is 1.1, $\sigma = 0.3$. Excluding two compounds with higher rates, the mean value of the ratios becomes 1.0 and $\sigma = 0.1$. We believe it highly unlikely that the two rate constants for every substrate are identical by pure coincidence. The authors make no comments on this nor do they draw it to the attention of the reader. Conversely, this result is of tremendous interest and has to be carefully considered when deriving kinetic mechanisms for the hydrolysis of phenylureas. We conclude that the proposed kinetic mechanisms should be reconsidered on the light of these comments.

References

1 R. Laudien and R. Mitzner, *J. Chem. Soc., Perkin Trans. 2*, 2001, 2230.
2 R. Laudien and R. Mitzner, *J. Chem. Soc., Perkin Trans. 2*, 2001, 2226.

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