# EFFECT OF HYDRATION ON KINETICS OF THERMAL DECOMPOSITION OF BENZENE DIAZONIUM CHLORIDE AT 25°C.

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The thermal decomposition of benzene diazonium chloride takes place via the equilibrium[1] $C_6H_5N_2^+$ ----> $C_6H_5^+ + N_2$. Although the reaction shows unimolecular first order kinetic with respect to $C_6H_5N_2Cl$, the dependence of the observed rate constant and percentage yield of $C_6H_5OH$ and $C_6H_5CL$ on the concentration of $C_6H_5N_2Cl$ and background HCl remains unexplained.

In the present investigation the observed rate constants (Kobs) were determined by measuring the volume of liberated nitrogen, at different time intervals and at different stirring speeds in the presence of 0-5 mol $dm^{-3}$ sodium chloride as the background electrolyte at 25°C. The increase of concentration of $C_6H_5N_2Cl$ or the background chloride lowers the water activity (aw) and increases the chloride activity ($aci^-$)[2]. In concentrated chloride solutions $aci^-$ is greater than aw and hence the yeild of $C_6H_5OH$ decreases and that of $C_6H_5Cl$ increases with increasing concentration of HCl or $C_6H_5N_2Cl$. The plot of log Kobs vs log aw shows a linear relationship with slope 3 and therefore the decrease in Kobs from the value at infinite dilution (Ka at aw=1) is related to the decrease in water activity: $Kobs = Ka\ (aw)^3$. In the case of stirred solutions the plot of logKobs vs logaw shows a linear relationship of slope 1. This observation and the increase in Kobs caused by stirring is related to the equation: $Kobs = Ko\ K\ aw/CN_2$ based on the equilibrium: $C_6H_5N_2(H_2O)^{3+}Cl^- \overset{K}{\rightleftharpoons} C_6H_5(H_2O)^+Cl^- + N_2 + 2h_2O$.

Results show that the decomposition reaction in stirred solutions takes place via $C_6H_5(H_2O)^+Cl^-$ and that ko >Ko. The decrease in solubility of nitrogen ($CN_2$) causes the positive deviations of logKobs from slope 1 at higher concentrations of NaCl (>3 mol $dm^{-3}$).

References: 1. N.Zolloinger, Pure Appl.Chem., 1983, 55 401.

2. G. Senanayake, and D.M.Muir, Electrochim.Acta, 1988, 33,3.