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The Role of Pyridine in the Bromination of Aromatic Compounds

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Pyridine (Py) is known to be a catalyst or "halogen-carrier" in electrophilic aromatic bromination[1]. But its exact role in the reaction does not seem to have been clearly understood. It is generally presumed that $PyBr^+$ could be the electrophilic brominating species[1]. Available kinetic experimental evidence on this point is rather meagre. Yeddanapalli and Gnanapragasam[2] found that the addition of small amounts of Py increased the rate of bromination of anisole in carbontetrachloride. Seshadri and Ganesan[3], while investigating the kinetics of the bromination of paradimethoxybenzene in dry acetic acid medium, did not, however, observe any catalytic effect due to added Py. Actually, the rate did not increase even when the concentration of the added Py equalled that of the reactants. We have, therefore, investigated this problem further.

Kinetic measurements were made on the bromination of anisole in the presence of varying amounts of initially added pyridine [Py] in dry acetic acid medium at 30°. The initial concentrations of anisole and bromine were $1{\cdot}0 \times 10^{-2} M$. [Py] was varied from zero to 3·7 M and in each case the third order rate constant (k_3) was calculated. (It has been shown that this reaction is of the third order[4]). Figure 1 shows the plot of k_3 against log

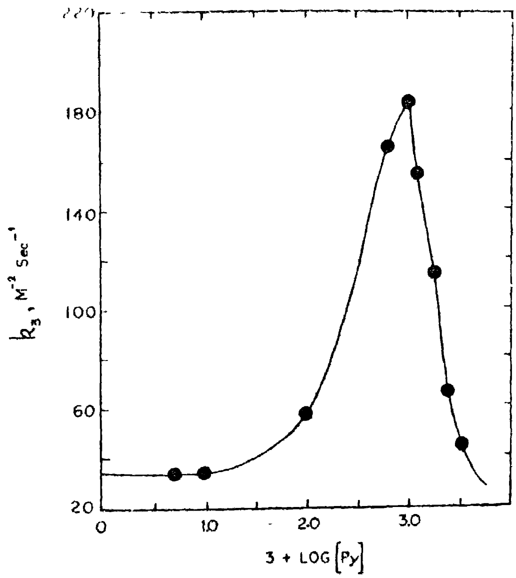

Fig. 1. Plot showing the effect of initially added pyridine on the rate of bromination of anisole in dry acetic acid at 30°C.

[Py]. It is seen that there is no increase in k_3 until $[Py] = 1{\cdot}0 \times 10^{-2} M$. With further gradual addition of [Py] the rate constant increases, a maximum is reached and then the rate rapidly decreases.

The above observation can be explained as follows. Pyridine and other amines like 2-picoline and 2,6-lutidine form addition compounds with halogens and interhalogen compounds[5,6]. These addition compounds also undergo ionization[7]. Thus Py and Br_2 form the complex $Py.Br_2$ which gives rise to the species $PyBr^+$ and Br^-.[1] We can therefore propose that

$$Py + Br_2 \overset{K}{\rightleftharpoons} PyBr^+ + Br^-$$

and

$$K = \frac{[PyBr^+][Br^-]}{[Py][Br_2]}$$

Both Br_2 and $PyBr^+$ can act as electrophilic brominating species. But the nature of the graph obtained indicates that Br_2 is the brominating species. The addition of small amounts of pyridine (up to $1{\cdot}0 \times 10^{-2} M$) does not produce any appreciable change in the medium. Further addition produces the ionic species $PyBr^+$ and Br^-. These species, along with the free Py, increase the dielectric or polar character of the medium. Hence, the rate increases, since the activated complex formed in the reaction is more polar than the reactants[3,8,9] and a maximum is reached. With further addition of Py, the polarity of the medium of course increases, but there are not enough molecules of free Br_2 to brominate the anisole, since most of them are present either in the form of $Py.Br_2$ or as $PyBr^+$. Therefore, the rate starts decreasing.

If $PyBr^+$ is the brominating species, the rate should continue to increase on the addition of more and more of Py and no maximum point will be obtained. We have therefore to conclude that Br_2 is the brominating species even in the presence of pyridine.

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