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Conductometric Studies of the Reaction of Pyridine and 3-Picoline with Iodine in Methanol

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Saxena and Gelra[1] investigated the reaction of some heterocyclic tertiary bases (pyridine, 3-picoline, quinoline, *etc.*) with acetone in methanolic medium; an extension of King's keto-alkylation reaction[2] to aliphatic ketones. They reported the formation of *N*-acetonylpyridinium and *N*-acetonyl-3-picolinium iodides in good yields. An immediate formation of the di-iodide[3] of the heterocyclic tertiary bases was first observed on mixing the base with iodine and acetone in methanol. The crystals of the di-iodide gradually disappeared on keeping for 2—3 days and crystals of the quaternary β-ketoalkyl iodide appeared. This prompted us to investigate the mechanism of formation of the di-iodides of the heterocyclic tertiary bases (pyridine and 3-picoline) and their subsequent reaction with methyl ketones resulting in the formation of quaternary β-ketoalkyl iodides. In the present investigation only the first part of the reaction, *i. e.* the reaction of pyridine and 3-picoline with iodine in methanol, has been studied through conductivity measurements. The latter part of the reaction with the methyl ketones will be reported elsewhere.

Experimental

Reagents Used. Analytical grade reagents were used. They were purified before use by standard methods. Every care was taken to use reagents in the reaction in the complete absence of moisture.

Procedure. A stock solution of iodine in absolute methanol was prepared. No change in conductivity values of this solution was observed the solution was preserved in a flask tightly stopped with ground glass. Fresh slutions of pyridine or 3-picoline in methanol containing 5—15% of the desired tertiary base were made in different flasks. This particular range was selected because in concentration of the base below 5%, the reaction was found to be very slow and the conductivity keeps on changing for more than 24 hr, whereas in concentrated solutions (base above 15%), the reaction becomes extremely fast and the conductivity changes are negligible after 15 min. Selected volumes of the solutions of iodine and the desired base were mixed in a tightly stoppered conductance cell, with the platinum electrodes immeresed in the reaction mixture. The cell was thermostated and the conductance values were recorded at temperatures 25, 30, 35, and 45°C. As the time of measurement was nearly 2 hr, no appreciable effect of the platinum electrodes on the resistance values was observed. Philips conductivity bridge was used for conductivity measurements.

The results are summarized in Tables 1—4.

Table 1. Effect of variation in concentration of pyridine on rate of reaction

$[I_2]=2.3425\times10^{-4}$M Temperature=303°K

No.	[Pyridine] M	$k'\times10^9$ sec^{-1}	Sp. rate constant $k'/[\text{Py}]\times10^9$ $l\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$
1	1.24	4.866	4.248
2	1.86	7.884	4.239
3	2.48	10.530	4.246

Table 2. Effect of variation in concentration of 3-picoline on rate of reaction

$[I_2]=2.5\times10^{-3}$M Temperature=303°K

No.	[3-Picoline] M	$k'\times10^9$ sec^{-1}	Sp. rate constant $k'/[\text{3-Pic}]\times10^9$ $l\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$
1	0.537	3.282	6.112
2	0.860	5.244	6.098
3	1.290	7.881	6.109

Table 3. Effect of variation in concentration of iodine on rate of reaction

[3-Picoline]=1.29M Temperature=303°K

No.	[Iodine], M	$k'\times10^9$, sec^{-1}
1	2.5×10^{-3}	7.881
2	3.5×10^{-3}	7.858
3	4.5×10^{-3}	7.846

Table 4. Effect of variation in temperature on rate of the reaction

$[I_2]$ in case of 3-picoline$=2.5\times10^{-3}$M
$[I_2]$ in case of pyridine$=2.3425\times10^{-4}$M

No.	Temperature °K	[3-Picoline]=1.29M $k'\times10^9$, sec^{-1}	[Pyridine]=1.24M $k'\times10^9$, sec^{-1}
1	298	4.995	2.966
2	303	7.881	4.866
3	308	10.353	7.416
4	318	15.777	11.544

Discussion

Neglecting the change of equivalent conductance with ionic strength, the reciprocal of resistance (R) was assumed to be proportional to the ionic concentration,[4] and a plot of $1/R$ against time gave a straight line. This linear relationship showed a zero-order of reaction with respect to iodine. The change in con-

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[1] J. P. Saxena and M. R. Gelra, *Aust. J. Chem.*, **20**, 1771 (1967).

[2] L. C. King, *J. Amer. Chem. Soc.*, **66**, 894 (1944).

[3] J. P. Saxena and M. R. Gelra, *Ind. J. Chem.*, **6**, 562 (1968).

[4] R. G. Pearson, *J. Amer. Chem. Soc.*, **69**, 3100 (1947).

centration of the base resulted in a corresponding change in the slope, thereby showing that the reaction is first order with respect to the base.

Saxena and Gelra[5] studied the reaction of pyridine with iodine in methanol and proposed the following mechanism:

$$\mathrm{MeOH \cdot I_2} + \mathrm{Py} \overset{K_1}{\rightleftharpoons} \mathrm{Py \cdot I_2} + \mathrm{MeOH} \quad \text{(fast)} \tag{1}$$

$$\mathrm{Py \cdot I_2} \overset{K_2}{\rightleftharpoons} [\mathrm{Py \cdot I}]^+ + \mathrm{I^-} \quad \text{(slow)} \tag{2}$$

We have studied the reactions of both pyridine and 3-picoline with iodine in methanol at different temperatures and have found that the general behavior of both the reactions is identical, and in the case of 3-picoline also the dissociation of 3-Pic$\cdot$I$_2$ is the rate determining step, as suggested in the case of pyridine.

$$\text{3-Pic} \cdot \mathrm{I_2} \overset{K_3}{\rightleftharpoons} [\text{3-Pic} \cdot \mathrm{I}]^+ + \mathrm{I^-} \quad \text{(slow)} \tag{3}$$

The thermodynamic data also confirm the identity of the behavior of the di-iodides of the two bases. From the specific rate constants obtained in the case of pyridine-iodine system, the activation energy was calculated to be 14.97 kcal/mol and the entropy change was evaluated as −8.69 e.u. In the case of 3-picoline-iodine system the activation energy was found to be 11.67 kcal/mol and the entropy change was evaluated as −10.4 e.u. This negative value of entropy change lends additional support to the proposed rate determining step, because as expected the dissociation would lower the entropy change appreciably in both cases. In the case of 3-picoline the hyperconjugative effect of the 3-CH$_3$ group is operative, due to which the dissociation of I$^-$ ions from 3-Pic$\cdot$I$_2$ takes place with greater ease and gives rise to the decrease in the entropy change (ΔS^* −10.4) as compared with pyridine (ΔS^* −8.69). With the existence of [Py$\cdot$I]$^+$ as [Py$_2\cdot$I]$^+$ apparently through solvation,[6] and of I$^-$ ions as I$_3^-$ ions, a negative entropy change is anticipated. This also holds true in the case of 3-picoline, and subscribes to the mechanistic step (3).

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[5] J. P. Saxena and M. R. Gelra, *Proceedings of the Symposium on Electrode Processes*, Jodhpur Univ., Nov. 1966, p. 157.

[6] I. Haque and J. L. Wood, *Spectrochim. Acta, Part A*, **23**(4), 959 (1967).