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### Polymerization of Acrolein by Several Cyclic Amines and Water System

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LETTER TO THE EDITOR

## Polymerization of Acrolein by Several Cyclic Amines and Water System

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Previous papers described how acrolein (I) could be polymerized by a mixture of pyridine and water below room temperature [1, 2]. Kinetic investigations revealed that the polymerization might be initiated by the hydroxyl anion formed through thermodynamic equilibrium between pyridine and water [3]. This observation suggest that amine basicity should play a role in the polymerizability of I.

The polymerization of I has therefore, been kinetically investigated in the presence of water and several cyclic amines such as pyridazine, pyrimidine, pyrazine, pyrazole, 1,2,4-triazole, benzimidazole, and imidazole. In every case the overall polymerization rate ( $R_p$ ) was determined by

$$R_p = [\text{amine}] [\text{H}_2\text{O}] [\text{I}]^2$$

by changing the concentrations of the monomer and the catalysts. This equation is the same as that for the pyridine system [3], indicating that the polymerization of I by all these cyclic amines might be initiated through the same mechanism.

Table 1 summarizes the observed rate constants and the relative rates.

TABLE 1. Observed Rate Constants ( $k$ ) and Relative Rates in the Polymerization of I by Several Cyclic Amines and Water at 0°C<sup>a</sup>

Amine	$k$ (liter mole <sup>-1</sup> min <sup>-1</sup> )	Relative rate ( $k/k_0$ )	$pK_a$ [4]
Pyrazine	$1.29 \times 10^{-5}$	1.00	0.60
Pyrimidine	$7.20 \times 10^{-5}$	5.54	1.30
Pyridazine	$3.62 \times 10^{-4}$	$2.77 \times 10$	2.33
Pyrazole	$2.18 \times 10^{-3}$	$1.54 \times 10^2$	2.53
1,2,4-Triazole	$6.41 \times 10^{-3}$	$4.62 \times 10^2$	2.55
Benzimidazole	$7.23 \times 10^{-3}$	$5.39 \times 10^2$	5.53
3-Bromopyridine [3]	$1.02 \times 10^{-2}$	$7.69 \times 10^2$	2.84
3-Acetylpyridine [3]	$1.20 \times 10^{-2}$	$9.23 \times 10^2$	3.18
3-Methylpyridine [3]	$2.83 \times 10^{-2}$	$2.15 \times 10^3$	5.68
Pyridine [3]	$1.83 \times 10^{-2}$	$1.38 \times 10^3$	5.17
4-Methylpyridine [3]	$4.91 \times 10^{-2}$	$3.77 \times 10^3$	6.02
Imidazole	$1.32 \times 10^{-1}$	$1.05 \times 10^4$	7.16

<sup>a</sup>The initial polymerization rate was estimated from the decreasing rate of I by means of gas chromatography [3]. Polymerization conditions: total volume, 10 ml; I, 0.78-1.54 mole/liter; amines, 0.01-0.10 mole/liter; water, 0.56-2.78 mole/liter; in tetrahydrofuran at 0°C.

It is interestingly to note that a linear relationship was obtained by plots of  $pK_a$  values of amines against the logarithm of the relative rate (Fig. 1).

This fact clearly indicates the dependence of polymerizability upon amine basicity, that is, the polymerization might be initiated by the hydroxyl anion formed through equilibrium between amine and water.

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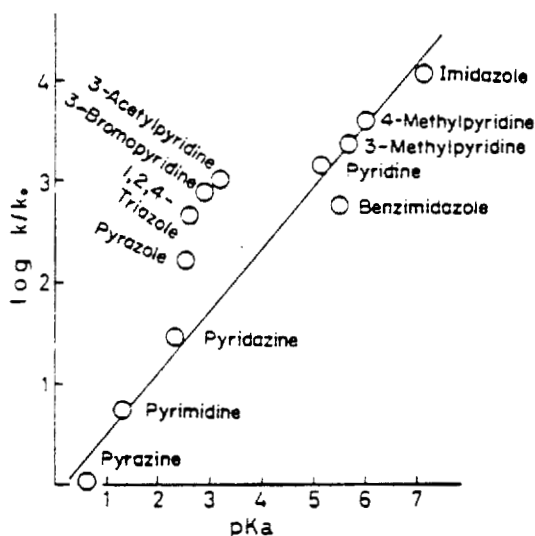


FIG. 1. Linear relationship between  $pK_a$  values of amines and  $\log k/k_0$ .

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