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Quaternization Kinetics. II. Pyridine and 4-Picoline in Propylene Carbonate[1]

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The quaternization at 25, 50 and 75° of pyridine and 4-picoline by *n*-butyl bromide in propylene carbonate (dielectric constant, 65.1) follows second-order kinetics; at 25°, $k_2 = 2.59 \times 10^{-4}$ and 4.7×10^{-4} for pyridine and 4-picoline, respectively. Values of ΔE are 16.40 and 16.25 kcal./mole and of $\Delta S^{\ddagger}$, −30.0 and −29.0. Rates are slower than in tetramethylene sulfone, which has a lower dielectric constant.

The quaternization of several pyridine bases in tetramethylene sulfone has been found[3] to follow second-order kinetics accurately. In this paper, it will be shown that pyridine and 4-picoline also follow the same kinetics in propylene carbonate. The latter is a stable solvent of fairly high dielectric constant (65 at 25°) and appears to be a useful medium for quaternization reactions.

Experimental

Materials.—Pyridine, 4-picoline and *n*-butyl bromide were refractionated samples of C.P. reagents. **Propylene carbonate** (4-methyldioxolone-2) was purchased from the Jefferson Chemical Company. It was purified by distillation; b.p. 92° at 4.5 mm. The density ρ was determined in a 20-ml. pycnometer; $\rho(25°) = 1.197$; $\rho(50°) = 1.171$; $\rho(75°) = 1.144$. The dielectric constant was measured at 100 kc. in a guarded cell[4]; the value found was 65.1 at 25°.

Method.—Briefly described, solutions of base and of butyl bromide (about 0.1 *M*) were made up by weight, mixed and sealed into 2–3-ml. ampoules which were then immersed in thermostats at 25, 50 or 75°. At appropriate intervals, a tube was taken from the bath, and opened. Most of the contents were withdrawn by a hypodermic syringe, and the sample was then injected into 45 ml. of methanol and 6 ml. of aqueous 2 *N* sulfuric acid for potentiometric titration with 0.005 *N* silver nitrate solution. The weight of the sample was determined by difference in syringe weights.

Results and Discussion

The experimental results are summarized in Table I which gives temperatures, concentrations (b = moles base per gram of initial reaction mixture, a = moles butyl bromide per gram) and second-order rate constants k_2 in units (liters/mole min.). The latter were obtained as before[3] from the analytical data. Up to about 80% quaternization (beyond which the experimental error increases quite rapidly), the reaction follows second-order kinetics as shown by the linearity of plots against time of $xa(a - x)$ for $a = b$ or $\ln[b(a - x)/a(b - x)]$ for $a \neq b$; here x is concentration of bromide ion produced at time t. There was evidence for a minor side reaction: at about half reaction at 50 or 75°, an orange color developed; as the reaction proceeded, the color deepened to brown. The same color sequence at about the same rate appeared when picoline was heated with propylene carbonate; since the rate constants nevertheless remained constant, this side reaction does not interfere with the quaternization.

TABLE I

QUATERNIZATION BY *n*-BUTYL BROMIDE IN PROPYLENE CARBONATE

t, °C.	$10^4 b$	$10^4 a$	$10^3 k_2$
	Pyridine		
25	1.674	1.198	0.258
25	0.940	1.068	0.260
50	2.236	1.063	2.25
50	0.993	0.993	2.22
75	1.013	0.974	13.85
75	0.662	1.854	13.85
	4-Picoline		
25	0.922	1.076	0.479
25	.841	2.160	0.461
50	.758	1.191	3.97
50	.962	2.594	3.83
75	.670	0.987	24.6
75	.994	2.419	24.0

TABLE II

REACTION CONSTANTS

Cpd.	log A	ΔE	$\Delta S^{\ddagger}_{298}$
C_5H_5N	8.44	16.40	−30.0
C_6H_7N	8.69	16.25	−29.0

The reaction constants are given in Table II; they are defined by the familiar equation $k_2 = A \exp(-\Delta E/RT)$ and $\Delta S^{\ddagger}_{298} = R \ln A - 68.69$. On comparing with the rates in tetramethylene sulfone,[3] both pyridine and picoline are seen to react faster in tetramethylene sulfone than in propylene carbonate, despite the higher dielectric constant of the latter solvent. The ratios of the rates at 75° for pyridine and for picoline, respectively, are 1.69 and 1.65; at 25°, 1.79 and 1.78.

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(2) Results presented in this paper will be included in a thesis to be presented by Paul L. Kronick to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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