[CONTRIBUTION NO. 1331 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Quaternization Kinetics. III. Pyridine and 4-Picoline in 2,4-Dimethylsulfolane[1]

BY ERNEST HIRSCH[2] AND RAYMOND M. FUOSS

RECEIVED AUGUST 19, 1955

The quaternization at 25, 50 and 75° of pyridine and 4-picoline by *n*-butyl bromide in 2,4-dimethylsulfolane follows second-order kinetics, with no evidence for side reactions. At 25°, $k_2 = 1.60 \times 10^{-4}$ for pyridine and 2.87×10^{-4} for 4-picoline. The values of ΔE are 16.45 and 16.25 kcal./mole and of $\Delta S^{\ddagger}$ are −31.0 and −30.4.

The hydrogenated addition product of 2-methyl-1,3-pentadiene and sulfur dioxide is available in commercial quantities (Shell Chemical Corporation). We have found that it is an excellent medium for quaternization reactions: it is chemically and thermally stable and shows no side reactions with the reagents. The purpose of this paper is to present the results of a study of the kinetics of quaternization by *n*-butyl bromide of pyridine and of 4-picoline in 2,4-dimethylsulfolane at 25, 50 and 75°.

Experimental

Materials.—Pyridine, 4-picoline and *n*-butyl bromide were redistilled samples of C.P. reagents. 2,4-Dimethylsulfolane, as received, contains a small amount of colored material; vacuum distillation (128° at 7 mm.) gave a water-white product. Densities were determined in a 20-ml. pycnometer: $\rho(25°) = 1.1314$, $\rho(50°) = 1.1106$, $\rho(75°) = 1.0896$. The dielectric constant, measured at 100 kc. and 25.00° in a guarded cell,[3] was found to be 29.5; unsubstituted sulfolane (tetramethylene sulfone) has a dielectric constant[4] of 42.0 at 50°.

Method.—Reaction mixtures were made up by weight and 2–3-ml. samples were sealed in ampoules which were then placed in thermostats at 25, 50 and 75°. Tubes were withdrawn for potentiometric determination of bromide ion at suitable intervals.[4] The time for 50% conversion is given by the equations

$$t_{1/2} = 1/k_2'a, \quad a = b \qquad (1)$$

and

$$t_{1/2} = \frac{\ln\,[(2a - b)/a]}{k_2'\,(a - b)}, \; a \neq b$$

where k_2' is in practical units, g./mole hr. To convert to k_2 in conventional units, l./mole min.

$$k_2' = 60000k_2$$

In eq. 1 and 2, *a* and *b* are initial concentrations of butyl bromide and nitrogen base in units moles reagent/g. reaction mixture.

Results and Discussion

The experimental results are summarized in Table I, which gives temperature, initial concentrations and second-order rate constants.

TABLE I

QUATERNIZATION BY *n*-BUTYL BROMIDE IN DIMETHYLSULFOLANE

t, °C.	10^4b	10^4a	10^3k_2
	Pyridine		
25	0.992	1.016	0.158
25	0.965	1.955	0.158
25	2.007	0.986	0.166
50	1.021	0.995	1.36
50	1.107	2.293	1.29
75	0.976	0.983	8.45
75	0.993	1.993	8.7
	4-Picoline		
25	0.997	1.001	0.294
25	1.126	2.021	0.280
50	1.011	1.158	2.43
50	0.982	2.049	2.42
75	0.977	0.965	15.3
75	0.968	1.955	14.2
75	1.230	1.606	15.0

TABLE II

REACTION CONSTANTS

Cpd.	log A	ΔE	$\Delta S^{\ddagger}_{298}$
C_5H_5N	8.24	16.45	−31.0
C_6H_7N	8.37	16.25	−30.4

The rate constants were obtained from the data by plotting $x/a(a - x)$ or $\ln[b(a - x)/a(b - x)]$ against time, where x is the concentration of bromide ion at time t. Beyond 80–90% conversion, the points began to scatter, due to sensitivity of the functions to small errors in x, but up to this range, the plots were linear, showing that the kinetics are second order.

The constants A and ΔE of the Arrhenius equation and the Eyring reaction entropy ΔS^{+} (298°K.) are given in Table II. The rates in dimethylsulfolane are about 0.37 times the rates in tetramethylene sulfone[4]; the sequence is that expected[5] from the dielectric constants of the two solvents. The temperature coefficient is higher in dimethylsulfolane while the statistical factor is smaller.

NEW HAVEN, CONNECTICUT

---

(1) Office of Naval Research Project NR 051-002, Paper No. 50. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government.

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

(3) H. Sadek and R. M. Fuoss, THIS JOURNAL, **76**, 5897 (1954).

(4) B. D. Coleman and R. M. Fuoss, *ibid.*, **77**, 5472 (1955).

(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 419–423.