

Rates of Aminolysis

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(1) National Science Foundation Fellow, 1952-1953. For further experimental data see D. C. Dittmer, Ph.D. Thesis, M.I.T., September, 1953.

Table I records first-order rate constants for the solvolysis of seven compounds in various amine solutions. The results are striking from the point of view of the Brønsted catalysis law for bases. The ratio of rate constants for *n*-butylamine and aniline is 13.0 for methyl bromide, 2.3 for *n*-butyl bromide, 0.89 for benzyl chloride, 0.0008 for benzhydryl chloride, and 10^{-5} for trityl thiocyanate. Thus the higher electrophilic reactivity of aniline outweighs its lower basicity and nucleophilic reactivity with the benzyl, benzhydryl and trityl compounds.

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Table I

RATES OF AMINOLYSIS

<u>Compound^a</u>	<u>Solvent^b</u>	<u>Temp., °C.</u>	<u>k₁, sec.⁻¹</u>
MeBr	Et ₃ N	50	1.56 x 10 ⁻⁴
"	n-BuNH ₂	50	1.00 x 10 ^{-1 c}
"	C ₅ H ₅ N	50	8.30 x 10 ⁻³
"	φNH ₂	50	7.66 x 10 ⁻³
"	φNMe ₂	50	2.69 x 10 ⁻⁴
n-BuBr	Et ₃ N	75	2.81 x 10 ⁻⁷
"	n-BuNH ₂	75	2.03 x 10 ⁻³
"	C ₅ H ₅ N	75	5.13 x 10 ⁻⁴
"	φNH ₂	75	8.79 x 10 ⁻⁴
"	φNHMe	75	2.57 x 10 ⁻⁴
"	φNMe ₂	75	3.79 x 10 ⁻⁶
"	m-ClφNH ₂	75	2.24 x 10 ⁻⁵
i-BuBr	n-BuNH ₂	50	2.92 x 10 ⁻⁵
"	C ₅ H ₅ N	50	3.15 x 10 ⁻⁶
"	φNH ₂	50	8.26 x 10 ⁻⁶
φCH ₂ Cl	Et ₃ N	50	7.55 x 10 ⁻⁸
"	n-BuNH ₂	50	1.12 x 10 ⁻³
"	C ₅ H ₅ N	50	1.28 x 10 ⁻⁴
"	φNH ₂	50	1.26 x 10 ⁻³
"	φNHMe	50	5.04 x 10 ⁻⁴
"	φNMe ₂	50	1.73 x 10 ⁻⁷
φ ₃ CHCl	Et ₃ N	25	< 10 ^{-10 d}
"	n-BuNH ₂	25	9.91 x 10 ⁻⁷
"	C ₅ H ₅ N	25	1.93 x 10 ⁻⁷
"	φNH ₂	25	1.20 x 10 ⁻³
"	φNHMe	25	2.31 x 10 ^{-4 e}
"	m-ClφNH ₂	25	1.03 x 10 ^{-2 f}

(Table I continued)

Compound	Solvent	Temp., °C.	k_1 , sec. ⁻¹
$\phi_3\text{CSCN}$	<u>n</u> -BuNH ₂	25	< 10 ⁻⁸ ^g
"	C ₅ H ₅ N	25	< 10 ⁻¹⁰ ^h
"	ϕNH_2	25	2.21 x 10 ⁻³

^a ϕ = C₆H₅ or p-substituted C₆H₄.

^b Me, Et, Bu = CH₃, C₂H₅, C₄H₉; C₅H₅N = pyridine. The solvent was always 95.2% amine - 4.8% benzene based on volumes before mixing.

^c Estimated from points beyond 90% reaction.

^d 1.3% reaction after 2.4 x 10⁵ min. (ca. 8 months).

^e Value is approximate because of analytical difficulties. (Oxidation of product to colored material obscured end points.)

^f Accurate to only about 20%. The reaction was difficult to follow because of its speed.

^g No appreciable reaction after 9.1 x 10⁴ min. (2 months).

^h No appreciable reaction after 3.3 x 10⁵ min. (7.5 months).

Table II lists some half-lives for the reaction of m-chloroaniline with benzhydryl chloride in benzene solution. The rate of reaction seems to be proportional to a higher than first power of the concentration of m-chloroaniline. Addition of small amounts of n-butylamine accelerated the reaction in spite of the fact that n-butylamine has a lower dielectric constant (5.3) than m-chloroaniline (13.3). This acceleration may be due to n-butylamine acting as a nucleophilic reagent while the m-chloroaniline behaves as an electrophilic reagent in a concerted "push-pull" process.

Table II

REACTION OF m-CHLOROANILINE AND BENZHYDRYL
CHLORIDE IN BENZENE AT 75°

<u>m-ClϕNH₂</u> <u>M</u>	<u>ϕ_2CHCl</u> <u>M</u>	<u>n-BuNH₂</u> <u>M</u>	Temp. °C	t 1/2 min.
1.061	0.092	—	75	420
0.237	.083	—	75	25,000
0.257	.121	—	75	19,000
0.252	.119	0.040	75	3,750

Experimental

Solvents.—n-Butylamine from Carbide and Carbon Chemical Co. was dried with calcium hydride and distilled through a 5-foot column, packed with glass helices, b.p. 78-79°, n_D^{25} 1.3950. The amine was stored in a glass-stoppered bottle over calcium hydride. Triethylamine from Sharples Chemicals Inc. was distilled from potassium hydroxide flakes through the 5-foot column, b.p. 91°. It was stored in a glass-stoppered bottle over calcium hydride.

Mallinckrodt reagent grade pyridine was distilled from sodium hydroxide through the 5-foot column, b.p. 114-115°. Eastman White Label m-chloroaniline was distilled, b.p. 228-229°, n_D^{25} 1.5932. Mallinckrodt reagent grade aniline was distilled from zinc dust through the 5-foot column, b.p. 184°. All were stored in a tightly capped brown bottle over calcium hydride and remained colorless for several months.

Other Materials.—Methyl bromide from the Westvaco Co., 99.5% pure, was used without further purification. n-Butyl bromide, Eastman white label grade, was dried over calcium hydride and distilled, b.p. 90.2-91°, n_D^{25} 1.4330. Benzyl chloride was Merck reagent grade used without further purification.

Benzhydryl chloride was prepared according to Gilman and Kirby from benzhydrol and thionyl chloride.² Benzhydrol was prepared according to

(2) H. Gilman and J. Kirby, J. Am. Chem. Soc., 48, 1733 (1926).

"Organic Syntheses" from benzophenone and zinc dust.³

(3) "Organic Syntheses," John Wiley and Sons, Ed. 2, 1941, Coll. Vol. 1, p. 90.

Kinetic Measurements.- In most of the aminolysis studies 40 ml. of amine was allowed to come to thermostat temperature, and ^{2 ml. of} a stock solution of the halide in dry benzene was added. Aliquots were taken as required. In slow reactions the reaction mixture was pipetted into soft glass test tubes which had been drawn out to give a neck for easy sealing. The tubes were sealed and placed in a constant temperature bath, one tube being opened at once and analyzed to give a zero-time point. In the reactions of methyl bromide with pyridine and triethylamine, smaller amounts of amine and halide were used; and, because of the speed of the reaction, a reaction was done for each point, the entire reaction mixture being quenched and the ionic halogen determined.

The reaction solutions were quenched in separatory funnels containing cold, 50% nitric acid and benzene. The benzene layer was extracted at least twice with water, and the aqueous solution of bromide or chloride was titrated by the Volhard method. In the determination of chloride, nitrobenzene was added after precipitation of silver chloride to coagulate the precipitate. All reaction vessels and pipets were dried before use.

Calculation of Rate Constants.- The rate constant, k_1 , for a first-order reaction is $-\frac{2.303}{t} \log (1-x)$ where t is the time and x is the fraction reacted. Values of k_1 for the aminolyses were obtained by plotting $10 \log (1-x)$ on a log scale vs. t on an arithmetic scale from which $k_1 = 0.693/\text{half-life}$. If the line plotted did not go exactly through the origin,

a line parallel to it which did was used, and the half-life was determined from the new line.

Determination of Products.- There is ample evidence in the literature that, at the temperatures used in this study, the primary halides, isobutyl and n-butyl bromide, do not yield olefins.⁴⁻⁶

(4) J. Semb and S. M. McElvain, J. Am. Chem. Soc., 53, 690 (1931).

(5) W. Drake and S. M. McElvain, ibid., 56, 1810 (1934).

(6) C. Noller and R. Dinamore, ibid., 54, 1025 (1932).

The kinetics indicated that the reaction of halides with primary amines gave only secondary amines, which was to be expected considering the large excess of amine over halide.

The product from the reaction of aniline and benzhydryl chloride was N-benzhydryl aniline which crystallized from ether as a resin, m.p. 47-50°. It was identified as its nitrate and hydrochloride, m.p. 155-156° and 201-203° respectively.⁷ On treatment with nitrous acid it gave a yellow-

(7) H. Gilman, J. P. Kirby and C. R. Kinney, ibid., 51, 2260 (1929); A. Skita, Ber., 48, 1696 (1915); W. E. Bachmann, J. Am. Chem. Soc., 53, 2674 (1931); M. Busch, Ber., 37, 2693 (1904).

green oil which gave a positive Liebermann's nitroso test.⁸ The product

(8) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., Ed. 3, 1948, p. 114.

gave no test for a primary amine after diazotization and treatment with β-naphthol.

The reaction of benzhydryl chloride with n-butylamine gave an amine which yielded a crystalline hydrochloride, m.p. 261-263°.

Anal. Calcd. for C₁₇H₂₂NCl (N-benzhydryl-n-butylamine hydrochloride): C, 74.02; H, 8.04; N, 5.08, Cl, 12.86. Found: C, 73.92; H, 8.02; N, 5.70; Cl, 12.28.

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