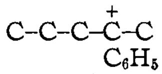
one hour at room temperature as the acid concentration increases from 92 to 97% (Table IV, runs 40, 41 and 42). Recovered unsulfonated hydrocarbon is negligibly isomerized. With (–)2-phenylpentane at two-thirds sulfonation the recovered hydrocarbon exhibits a slight loss of rotation, 3.6%, but no isomerization. If either 2- or 3-phenylpentane is sulfonated, and the sulfonic acid is then desulfonated by hydrolysis with phosphoric acid at 170°, unisomerized phenylpentane results (runs 44 and 45). With 2-phenylpentane, the total loss in rotation occurring during sulfonation and desulfonation was but 9.7%.

Thus, sulfonation is substantially faster than reactions 1 to 5. Once the sulfonic acid group is added, it induces a positive charge on the aromatic ring which stabilizes it against proton addition and presumably against formation of a benzylic carbonium ion. Such phenylpentanesulfonic acids are more stable than tetramethyl- and tetraethylbenzenesulfonic acids since these undergo the Jacobsen reaction.[24] Trimethyl- and triethylbenzenesulfonic acids, however, are stable in the presence of sulfuric acid.[24] On the other hand, di-*t*-butylbenzene and benzene react in the presence of sulfuric acid to form *t*-butylbenzene and *t*-butylbenzenesulfonic acid.[25] Greater ease of dealkylation of *t*-butyl groups and, perhaps, steric resistance to sulfonation may be involved. The possibility of intramolecular isomerization of the di-*t*-butylbenzene was not examined.[25]

Cram[26] reported that action of sulfuric acid on 2-phenylpentane caused a loss of rotation of 2% under conditions where sulfonation seems to have proceeded to about 10%.

If oxidation of the phenylpentane to form a benzylic carbonium ion is slow compared to sulfonation, it might be possible to augment racemization by addition of olefin, the addition of a proton to which would form a suitable carbonium ion. Indeed, Cram observed that addition of about 20% of olefins of the same skeleton to a mixture of 2- and 3-phenylpentane resulted in a 23% loss of rotation. Olefin is effective only during the first few moments since it is removed rapidly, apparently largely by polymerization (run 49, Experimental section).

Runs 46 and 47 show that olefin does not induce isomerization. Thus the ion  $\mathrm{C{-}C{-}C{-}\underset{C_6H_5}{\overset{+}{C}}{-}C}$ must be assumed to isomerize at a rate negligible in comparison to that of hydride ion transfer. This accords with the similar conclusion reached with aluminum chloride.

Slow epimerization of *dl*-2,3-diphenylbutane to the *meso* isomer accompanied by much more rapid sulfonation has been reported.[20]

Acknowledgment.—This work was supported by the Office of Naval Research.

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[24] L. I. Smith, "Organic Reactions," Vol. 1, R. Adams, Editor-in-chief, John Wiley and Sons, Inc., New York, N. Y., 1942, Chapter 12.

[25] V. N. Ipatieff and B. B. Corson, THIS JOURNAL, **59**, 1417 (1937).

[26] D. J. Cram, *ibid.*, **74**, 2152 (1952).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF OBERLIN COLLEGE]

A Kinetic Study of the Aminolysis and Hydrolysis of α-Naphthyl Acetate

BY PETER J. HAWKINS AND IVAN PISCALNIKOW

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A kinetic study of the reaction of *n*-butylamine with α-naphthyl acetate in aqueous solution is reported. The rate of disappearance of ester by simultaneous aminolysis and hydrolysis is in agreement with the equation $-\mathrm{d(ester)}/\mathrm{d}t = k_4\mathrm{(ester)(RNH^-)} + k_5\mathrm{(ester)(RNH_2)(H^+)} + k_2\mathrm{(ester)(OH^-)}$ (1). The similarity of aminolysis and hydrolysis in the form of their kinetic equations is indicated.

A kinetic study of the aminolysis of two thiol esters in aqueous solution has previously been reported[1] and it was shown that an equation involving at least the following terms was applicable

$$\text{rate} = k\mathrm{(ester)(RNH_2)(OH^-)} + k\mathrm{(ester)(OH^-)} \quad (1)$$

The first term was identified with the aminolysis and the second with the hydrolysis of the ester.

It was the purpose of the work presently reported to extend the investigation to oxygen esters, to demonstrate the third-order reaction previously observed and to confirm, if possible, the inclusion of the hydroxide ion concentration by the introduction of hydroxide ion from a source other than that of the hydrolysis of the amine.

The problems of defining the concentrations of kinetically significant species were met firstly, by the use of aqueous solutions for which the constants governing the interaction of amine and solvent are known and secondly by determining pseudo first-order rate factors under conditions where the amine was in large excess and could be assumed to remain essentially constant during the course of reaction. In view of the low concentrations necessary to retain a reasonable rate of reaction a spectrophotometric method of analysis was used to follow the course of the reaction. The ester α-naphthyl acetate was chosen because of its susceptibility to this method of analysis.

Previous investigations[2] of the aminolysis of oxygen esters have been largely confined to non-aqueous or part-aqueous solutions and in consequence some ambiguity must remain where the equilib-

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[1] P. J. Hawkins and D. S. Tarbell, THIS JOURNAL, **75**, 2982 (1953).

[2] (a) R. L. Betts and L. P. Hammett, *ibid.*, **59**, 1569 (1937); (b) M. Gordon, J. G. Miller and A. R. Day, *ibid.*, **70**, 1946 (1948); (c) E. M. Arnett, J. G. Miller and A. R. Day, *ibid.*, **72**, 5635 (1950); (d) R. Baltzly, I. M. Berger and A. A. Rothstein, *ibid.*, **72**, 4149 (1950); (e) T. A. Koch, J. G. Miller and A. R. Day, *ibid.*, **75**, 953 (1953).

rium constants for the amine–solvent interactions are unknown. This is evidenced in the second-order rate factors from equation 2 which show marked

$$\text{rate} = k(\text{ester})(\text{amine}) \qquad (2)$$

drifts to lower values as the reaction proceeds.

It was hoped in this investigation to avoid such ambiguity.

Experimental

α-Naphthyl Acetate.—α-Naphthyl acetate was prepared according to a method previously described.[3] The product was purified by repeated recrystallization from aqueous methanol and dried under vacuum; m.p. 50°.

α-Naphthol.—Technical grade α-naphthol obtained from the Eastman Kodak Co. was purified by adsorption of colored impurities on activated charcoal from aqueous methanol, and repeated recrystallization; m.p. 94°.

n-Butylamine.—n-Butylamine was obtained from the Eastman Kodak Co. and purified by fractional distillation to a 1° boiling range. The molar extinction coefficients of α-naphthyl acetate and α-naphthol were measured at 307 and 273 mμ in aqueous solution and the following data obtained.

	ϵ_{307} mμ	ϵ_{273} mμ
α-Naphthyl acetate	4.53×10^2	5.27×10^3
α-Naphthol	3.47×10^3	3.11×10^3

Analysis of known mixtures of α-naphthyl acetate and α-naphthol by the determination of the optical density at the two wave lengths and the solution of the simultaneous equations gave agreement within 1%.

A measured quantity of ester solution was placed in the reaction vessel (a 300-ml. round bottomed flask) which had previously been flushed with dry nitrogen. The amine or hydroxide solution was measured into a glass bulb of 30–50 ml. capacity having a long stem which protruded through the neck of the reaction flask. After thermal equilibrium was obtained, the inner bulb was broken to start the reaction. Aliquots were withdrawn at suitable intervals and run into an excess of hydrochloric acid and, after suitable dilution, were analyzed spectrophotometrically.

By analysis for α-naphthol spectrophotometrically the reaction (presumably both aminolysis and hydrolysis) was shown to proceed to within experimental error of 100%.

Discussion of Results

The significant results for the aminolysis reaction with or without added hydroxide and for the hydrolysis are given in Table I. In all cases pseudo first-order rate factors are given as the amine or hydroxide ion was maintained in large excess.

Representative runs for the aminolysis and hydrolysis are given in Table II and illustrate the constancy of the rate factors during the course of the reaction. The data for the aminolysis reaction without added hydroxide ion were first obtained and treated according to the equation used in the previous investigation.[1]

$$\text{Rate} = k_1(\text{RNH}_2)(\text{ester})(\text{OH}^-) + k_2(\text{ester})(\text{OH}^-)$$

For pseudo first-order constants, *i.e.*, first order in ester, the observed rate constant k_{obs} is given by the following equation

$$k_{\text{obs}} = k_1(\text{RNH}_2)(\text{OH}^-) + k_2(\text{OH}^-)$$

where k_2 is the second-order constant for the hydrolysis reaction and may be separately determined from the hydrolysis experiments.

TABLE I

SUMMARY OF HYDROLYSIS AND AMINOLYSIS DATA

A. Aminolysis

Run no.	(ester), mole/l. × 10^4	$(\text{RNH}_2 + \text{RNH}_3^+)_3$, mole/l. × 10^3	(OH^-), mole/l. × 10^3 from amine	added	k_{obs} × 10^3, sec.$^{-1}$
11	1.77	3.95	0.746		0.354
12	1.06	2.54	.584		.258
14	1.03	5.09	.858		.433
15	0.946	7.63	1.07		.597
16	.969	5.78	.920		.494
17	.976	4.34	.786		.396
18	1.42	9.94	1.23		.767
19	1.42	7.95	1.09		.626
21	1.16	11.93	0.894	1.25	1.18
22	1.31	7.95	.443	2.51	1.21
23	1.38	3.98	.382	1.25	0.579
24	1.17	11.93	1.36		0.932
27	.863	9.92	0.537	2.51	1.43
28	1.08	5.96	.343	2.51	1.08
30	1.07	2.15	.226	1.25	0.454
31	1.11	2.27	.344	0.627	.336
33	2.47	2.44	.519	0.125	.259
34	2.45	2.50	.578		.245

B. Hydrolysis

Run no.	(ester), mole/l. × 10^4	(OH^-), mole/l. × 10^3	k_{obs}, sec.$^{-1}$	$k$obs/(OH^-), l. mole^{-1} sec.$^{-1}$
4	1.08	2.72	0.536	0.197
5	2.03	3.40	.691	.203
6	0.976	3.40	.692	.204

TABLE II

REPRESENTATIVE RUNS

Hydrolysis of α-naphthyl acetate at 0°, run 6, (OH^-), 3.40 × 10^{-3} mol/l.

Time, sec.	(ester), mole/l. × 10^4	k_{obs} × 10^3, sec.$^{-1}$
0	0.976	
345	.755	0.744
569	.666	.673
1000	.482	.705
1470	.350	.697
1958	.265	.665
2935	.136	.670

Aminolysis of α-naphthyl acetate at 0°, run 11, $(\text{RNH}_2 + \text{RNH}_3^+)$, 3.95 × 10^{-3} mole/l.

Time, sec.	(ester), mole/l. × 10^4	$k_{\text{obs.}}$ × 10^{-3}, sec.$^{-1}$
0	1.77	
282	1.61	0.336
758	1.36	.352
1293	1.10	.368
2011	0.856	.362
2852	.621	.368
3991	.443	.347
5306	.285	.345

It should be noted that (RNH_2) represents the concentration of the unprotonated amine and is distinct from the total amine concentration $(\text{RNH}_2 + \text{RNH}_3^+)$. This concentration was calculated using an extrapolated value for base constant K_b for butylamine,[4] a value considered more accurate than that previously used.[1] The intercept from the plot of $k_{\text{obs}}/\text{OH}^-$ *versus* (RNH_2) (Fig. 1) was found to be approximately twice that expected from the separately determined hydrolysis constant. The linearity of the plot indicated that a further term was involved which under these conditions remained

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(3) F. D. Chattaway, *J. Chem. Soc.*, 2495 (1931).

(4) N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

constant. Thus the equation plotted might read

$$\frac{k_{obs}}{(OH^-)} = k_1(RNH_2) + k_2 + k_3\frac{(X)}{(OH^-)}$$

In the aqueous solution of the amine $(OH^-) = (RNH_3^+)$ and (X) could therefore be identified with either of these concentrations and meet the requirements of a linear plot with an intercept equal to $k_2 + k_3$.

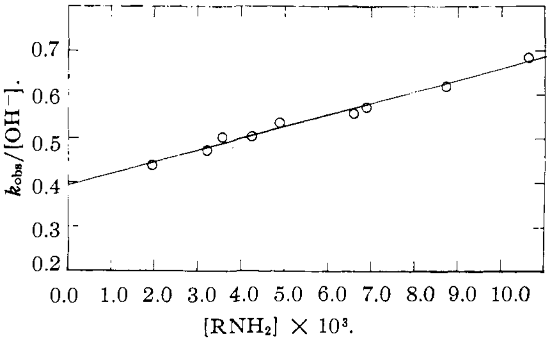

Fig. 1.

To distinguish between these two possibilities the $RNH_3^+:OH^-$ ratio was varied by the addition of sodium hydroxide and the equation plotted in a somewhat different form.

Assuming the equation to be of the form

$$k_{obs} = k_1(RNH_2)(OH^-) + k_2(OH^-) + k_3(RNH_3^+) \quad (3)$$

this may be transformed into the equation

$$\frac{k_{obs}}{(RNH^+_3)} - \frac{k_2(OH^-)}{(RNH_3^+)} = k_1\frac{(RNH_2)(OH^-)}{(RNH_3^+)} + k_3$$

and plotted accordingly to obtain k_1 and k_3.

All concentrations may be determined and k_2 is the rate factor determined in the hydrolysis experiments. The plot is shown in Fig. 2. The equation plotted no longer relies on the coincidental equality of the hydroxide and ammonium ion concentrations and includes those runs in which these concentrations were different. The linearity of this plot is taken as evidence of the validity of equation 3. It serves to confirm both the inclusion of (OH^-) as distinct from (RNH_3^+) in the first term of the equation, an ambiguity that remained in the thiol ester investigation[1] and to distinguish (RNH_3^+) from (OH^-) in the third term.

It must be remembered that the equation as written is not unique but that any other equation proposed should be transformable by the inclusion of suitable constants into equation 3. In such a manner the equation may be written

$$\text{rate} = k_4(\text{ester})(RNH^-) + k_2(\text{ester})(OH^-) + k_5(\text{ester})(RNH_2)(H^+)$$

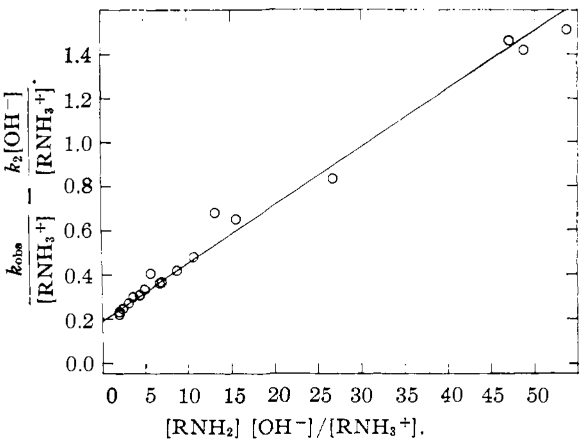

Fig. 2.

through the inclusion of the equilibrium constants of the equilibria

$$RNH_2 + OH^- = RNH^- + H_2O \quad (4)$$

$$RNH_2 + RNH_2 = RNH^- + RNH_3^+ \quad (5)$$

$$RNH_2 + H_2O = RNH_3^+ + OH^- \quad (6)$$

$$H^+ + OH^- = H_2O \quad (7)$$

Either 4 or 5 will allow the factor $(RNH_2)(OH^-)$ to be written as (RNH^-) and 6 and 7 allow the substitution of $(RNH_2)(H^+)$ for (RNH_3^+).

The substitution for these terms gives an equation which, in the terms applicable to the aminolysis, is similar to the corresponding equation for hydrolysis. Thus, in the alkaline hydrolysis, an equation $v = k(\text{ester})(OH^-)$ applies and in this representation of the aminolysis where $v = k(\text{ester})(RNH^-)$, the RNH^- ion has the role of the hydroxyl ion in the corresponding hydrolysis. The participation of the NH_2^- ion in the ammonolysis of phenyl acetate has been proposed by Betts and Hammett[2a] whereas Day, *et al.*,[2] prefer to interpret their data, in part or non-aqueous solutions, in terms of a loosely hydrogen-bonded complex between the ammonia or amine and the hydroxylic solvent.

In the acid-catalyzed reactions, the two equations are

$$v = k(\text{ester})(H_2O)(H^+) \text{ and } v = k(\text{ester})(RNH_2)(H^+)$$

for the hydrolysis and aminolysis, respectively, and the unprotonated amine, RNH_2, has the role of the water.

The choice of these terms in the final equation is, of course, arbitrary on the basis of the information at present available but it is, however, attractive in the light of the parallel hydrolysis reactions.

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