THE HYDROLYSIS OF ACETANILIDE.

BY DAVID R. MERRILL AND ELLIOT Q. ADAMS.

The acetylation of aniline has been studied by Menschutkin[1] and by Goldschmidt and Wachs,[2] but their experiments were made for the most part in glacial acetic acid or in aniline, hence the laws of aqueous solutions could not be expected to hold. The hydrolysis of acetanilide in alkaline solution has been studied by Davis.[3] While the hydrolysis of other anilides and acetyl compounds in acid solution has been studied, little has been done on the hydrolysis of acetanilide, which is probably the most important. For these reasons it was thought worth while to measure the rates of reaction and equilibria concerned in a fairly dilute acid solution.
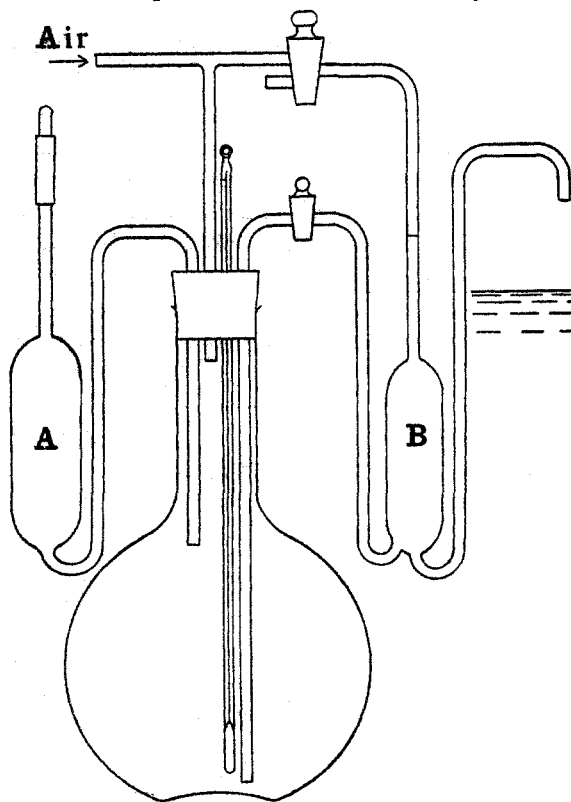

Fig. 1.

Experimental Work.—The progress of the reaction was followed by determining the total acidity by titration. In the acetylation experiments solutions were made up of aniline and acetic acid, and measured out with a pipet into glass tubes which were then exhausted to about 25 mm. and sealed. The tubes were placed in a thermostat at 100°, heated the requisite length of time, opened and the contents washed out and titrated. In the hydrolysis with acetic acid alone, the same amount of acetanilide was weighed out into each tube and a pipetful of acid added, since acetanilide is not

[1] Menschutkin, *Chem. Zentr.*, **1906**, I, 551.
[2] H. Goldschmidt and C. Wachs, *Z. phys. Chem.*, **24**, 353 (1897).
[3] O. M. C. Davis. *J. Chem. Soc.*, **95**, 1397 (1909).

soluble enough at room temperature to permit the making up of a solution of suitable concentration.

In the case of the hydrolysis in the presence of hydrochloric acid the reaction proceeds so much faster that it was found more convenient to use the apparatus shown in Fig. 1. The water and acetanilide were placed in the flask and the hydrochloric acid in the pipet A. After the whole had come to the temperature of the bath and the acetanilide was all dissolved, the acid was blown over into the acetanilide solution and thoroughly mixed. Then by turning the stopcocks in the proper sequence a pipetful of the solution could be blown out for analysis. By always running the solution into the same amount of cold water and titrating immediately, fair uniformity of the conditions was obtained. Because of the method of calculation used, the actual time from the beginning was not so important as uniformity in the measurement of the time of drawing the sample.

Method of Calculation.—We shall consider first the simplest case, namely, the hydrolysis in the presence of hydrochloric acid. Since at the concentration of acid present throughout the experiments the ionization of acetic acid and the "hydrolysis" of aniline hydrochloride are largely repressed—while the concentration of acetanilide hydrochloride is negligible—the ionic equation for the reaction studied is

$$C_6H_5NHCOCH_3 + H_2O + H^+ \longrightarrow C_6H_5NH_3^+ + CH_3COOH.$$
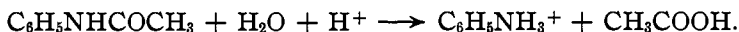
As the concentration of the water (more correctly its activity) does not change materially, the reaction may be expected to have the character of a bimolecular reaction, the rate being proportional to the product of the concentrations of acetanilide and hydrogen ion. (Under the experimental conditions the reverse reaction is entirely negligible.) The equations for the progress of such a reaction are

$$dx = k_2(a - x)(b - x)dt$$

$$2.303 \log \frac{b - x}{a - x} = (b - a)k_2t + 2.303 \log \frac{b}{a}$$

where a, b and x are, respectively,[1] the acid and acetanilide originally present, and the amount of each which has been used up at time t. The correction that must be made for the hydrogen ion furnished by the acetic acid and by the aniline ion is as follows: The ionization constant of acetic acid[2] at $100°$ is 1.11×10^{-5}, that of aniline ion[3] 3.1×10^{-4}, so that a mixture of equivalent amounts of the two in the presence of excess mineral acid will give as much hydrogen ion as one equivalent of an acid of constant 3.2×10^{-4}. If y represents the hydrogen ion so produced

[1] The notation differs from that used later in the paper in the calculation of the experiments in acetic acid solution.

[2] A. A. Noyes. THIS JOURNAL, **30**, 335 (1908).

[3] Determined colorimetrically, using methyl orange as an indicator.

$$3.2 \times 10^{-4}(HA) = (A^-)(H^+)$$
$$3.2 \times 10^{-4}(x - y) = y(a - x + y)$$

or
$$y = \frac{3.2 \times 10^{-4}(x - y)}{a - x + y}$$

from which y may readily be calculated by approximation. Since the rate of the reaction is directly proportional to the hydrogen-ion concentration, correction for the extra hydrogen ion y may be made by increasing all measured time intervals in the ratio of $1 + \dfrac{y}{a - x}$ to 1. In Fig. 2, $\log \dfrac{b - x}{a - x}$ has been plotted against the "effective time," and from the slope m of the
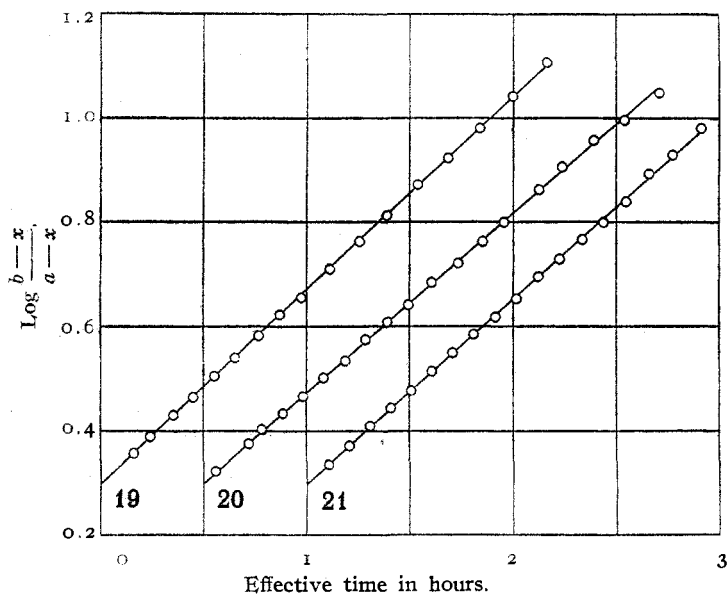

Fig. 2.

straight lines on these plots, the constant k_2 of the hydrolysis reaction has been calculated by the equation

$$k_2 = \frac{2.303 \, m}{b - a}.$$

The data and calculations are given in Tables 2 and 3.

When the reaction takes place in acetic acid solution the speeds of the reaction in the two directions are comparable and the hydrogen ion from the aniline salt and acetic acid, instead of being a small addition to that already present, constitutes the entire hydrogen-ion concentration of the solution. In addition the aniline and acetic acid are no longer present in equivalent amounts. The equation for the progress of the reaction

$$CH_3COOH + C_6H_5NH_3^+ \rightleftharpoons C_6H_5NHCOCH_3 + H_2O + H^+,$$

since the activity of the water is substantially constant, takes the form

$$dx = [k_1(CH_3COOH)(C_6H_5NH_3{}^+) - k_2x(H^+)]dt \qquad (I)$$

where x represents the concentration of acetanilide. If a and b be, respectively, the total acetic acid and aniline, each *including* acetanilide, and x the acetanilide present at time t, this equation can be put, according to the direction in which the reaction is proceeding, into the forms

$$\frac{dx}{(a-x)(b-x)} =$$

$$k_1\left[\frac{(CH_3COOH)(C_6H_5NH_3{}^+)}{(a-x)(b-x)} - \frac{k_2}{k_1}\frac{x(H^+)}{(a-x)(b-x)}\right]dt \qquad (II_1)$$

$$-\frac{dx}{x} = k_2\left[(H^+) - \frac{k_1}{k_2}\frac{(CH_3COOH)(C_6H_5NH_3{}^+)}{x}\right]dt. \qquad (II_2)$$

TABLE I.

$$C_6H_5NH_2 + CH_3COOH = C_6H_5NHCOCH_3 + H_2O.$$
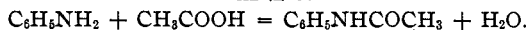
No.	Dir.[1]	ΣAn.	ΣAc.	(HCl).	Remarks.	No.	Dir.	ΣAn.	ΣAc.	(HCl).	Remarks.
1	→	0.1	0.2	...	Aniline too dilute	11	→	0.3	1.0	...	Duplicate of 5
2	→	0.1	0.5	...	Same	12	→	0.3	1.5	...	Duplicate of 6
3	→	0.1	1.0	...	Same	13	⇄	0.3	0.7	...	See Table 6
4	→	0.3	0.5	...	Acid too dilute	14	⇄	0.3	1.0	...	See Table 6
5	→	0.3	1.0	...	See Table 4	15	⇄	0.3	1.5	...	See Table 6
6	→	0.3	1.5	...	See Table 4	16	←	0.2		0.1	See Table 2
7	←	0.3	0.7	...	See Table 5	17	←	0.2		0.1	See Table 2
8	←	0.3	1.0	...	See Table 5	19[2]	←	0.2		0.1	See Table 2
9	←	0.3	1.5	...	See Table 5	20	←	0.2		0.1	See Table 2
10	→	0.3	0.7	...	See Table 4	21	←	0.2		0.1	See Table 2

The mass-law equations for acetic acid and aniline ion take the form

$$CH_3COOH = CH_3COO^- + H^+ \qquad K_A = \frac{(CH_3COO^-)(H^+)}{(CH_3COOH)} \qquad (IIIa)$$

$$C_6H_5NH_3{}^+ = C_6H_5NH_2 + H^+ \qquad K_B' = \frac{(C_6H_5NH_2)(H^+)^3}{(C_6H_5NH_3{}^+)} \qquad (IIIb)$$

whence, since

$$(CH_3COO^-) + (CH_3COOH) = a - x \qquad (IVa)$$

and

$$(C_6H_5NH_2) + (C_6H_5NH_3{}^+) = b - x, \qquad (IVb)$$

$$\frac{(CH_3COOH)}{a - x} = \frac{(H^+)}{K_A + (H^+)} \qquad (Va)$$

$$\frac{(C_6H_5NH_3{}^+)}{b - x} = \frac{(H^+)}{K_B' + (H^+)}. \qquad (Vb)$$

[1] The arrow shown is to be substituted for the = sign in the equation.

[2] Series 18 was lost because the acetanilide was not all in solution.

[3] This is not the usual K_B of aniline, but its reciprocal multiplied by the dissociation constant of water. As no data were available for this temperature, we have determined K_B' at 100° for aniline to be 3.1×10^{-4}.

TABLE 2.

No.		Series 19.							Series 20.		Series 21.	
	$t.$ H : m : s.	NaOH. Cc.	$x.$ Mol/l.	Log $b-x/a-x$.	100 y.	Mean $y/a-x.$	$\Delta t(1+y/a-x).$ Min.	$t'.$ Min.	$t.$ H : m : s.	NaOH. Cc.	$t.$ H : m : s.	NaOH. Cc.
0..........	2:54:00	20.13	..	..	...			..	2:34:00	20.13	1:48:30	23.02
						0.000	9.67					
1..........	3:03:40	24.60	0.0218	0.3582	0.009			9.67	2:37:40	22.01	1:55:00	26.46
						0.002	5.26					
2..........	3:08:55	26.51	0.0313	0.3910	0.015			14.93	2:47:00	25.70	2:01:00	29.12
						0.003	6.18					
3..........	3:15:10	28.40	0.0406	0.4301	0.022			21.11	2:51:00	27.19	2:07:00	31.25
						0.005	6.03					
4..........	3:21:05	29.83	0.0476	0.4655	0.030			27.14	2:57:00	28.59	2:13:00	33.11
						0.007	6.04					
5..........	3:27:05	31.12	0.0540	0.5041	0.038			33.18	3:03:00	29.96	2:19:00	34.59
						0.010	6.06					
6..........	3:35:05	32.16	0.0591	0.5404	0.046			39.24	3:09:00	31.13	2:25:00	35.87
						0.014	7.02					
7..........	3:40:00	33.19	0.0641	0.5822	0.057			46.26	3:15:00	32.08	2:31:00	36.97
						0.019	6.11					
8..........	3:46:00	33.98	0.0680	0.6204	0.068			52.37	3:21:10	33.04	2:37:00	37.94
						0.025	6.15					

9..........	3:52:00	34.60	0.0711	0.6553	0.078			58.52	3:27:00	33.78	2:43:00	38.74
						0.034	8.27					
10..........	4:00:00	35.43	0.0752	0.7093	0.095			66.79	3:33:10	34.43	2:49:00	39.49
						0.046	8.37					
11..........	4:08:00	36.09	0.0783	0.7581	0.112			75.16	3:40:00	35.18	2:55:00	40.26
						0.062	8.50					
12..........	4:16:00	36.64	0.0811	0.8099	0.131			83.66	3:47:00	35.61	3:01:00	40.76
						0.088	8.70					
13..........	4:24:00	37.21	0.0840	0.8774	0.157			92.36	3:54:00	36.19	3:07:00	41.27
						0.118	8.94					
14..........	4:32:00	37.61	0.0859	0.9248	0.178			101.30	4:00:00	36.59	3:13:00	41.70
						0.152	9.22					
15..........	4:40:00	37.97	0.0876	0.9771	0.201			110.52	4:09:00	37.10	3:19:00	42.17
						0.202	9.62					
16..........	4:48:00	38.31	0.0894	1.0426	0.229			120.14	4:15:00	37.53	3:25:00	42.67
						0.269	10.15					
17..........	4:56:00	38.62	0.0909	1.1079	0.258			130.29	4:23:00	37.84	3:31:00	42.94
18..........	...	...	..	..	...			..	4:31:00	38.05	3:37:00	43.37
19..........	...	...	..	..	...			..	4:39:00	38.33	...	...

Initial concentration HCl, a = 0.0993.
Initial concentration acetanilide, b = 0.1986.
Decrease, x, in the concentrations of HCl and of acetanilide calculated from volume of NaOH by the equation $x = p(V - V_0)$ where for series 19 and 20, p = 0.004924 and for series 21, p = 0.004313.

<div align="center">TABLE 3.</div>

Series No.	Slope. recip. hr.	k_2, 1/mol × hr.	Temp. obs.	Barometer. in. (of Hg).	Temp. calc.
19...................	0.3725	8.64	100.3°	29.97	100.05°
20...................	0.349	8.10	99.7°	29.81	99.90°
21...................	0.352	8.17	99.5°	29.45	99.55°
Mean................	..	8.30	99.83°	...	99.83°
Reduced.............	..	8.43	...	...	100.00°

Series 16 and 17 were performed in an oil thermostat and gave for k_2, 7.46 and 7.92, respectively. An investigation into the cause of this discrepancy showed that the thermostat regulator was not operating satisfactorily. The subsequent experiments were performed in a boiling water bath and the result reduced to 100°, assuming a $2^1/_2$-fold increase for 10°.

Substituting in Equations (II$_1$) and (II$_2$), since $k_1/k_2 = K$, the equilibrium constant for the acetylation of aniline (determined in separate experiments, see Table 6),

$$\frac{dx}{(a-x)(b-x)} = k_1\left[\frac{(H^+)^2}{(K_A + (H^+))(K'_B + (H^+))} - \frac{1}{K}\frac{x(H^+)}{(a-x)(b-x)}\right]dt \quad (VI_1)$$

$$-\frac{dx}{x} = k_2\left[H^+ - K\frac{(a-x)(b-x)}{x}\frac{(H^+)^2}{(K_A + (H^+))(K'_B + (H^+))}\right]dt \quad (VI_2)$$

or

$$\frac{2.303}{b-a}\log\left(\frac{b-x}{a-x}\right) = k_1\int\left[\frac{(H^+)^2}{(K_A + (H^+))(K'_B + (H^+))} - \frac{1}{K}\frac{x(H^+)}{(a-x)(b-x)}\right]dt + \frac{2.303}{b-a}\log\frac{b}{a}. \quad (VII_1)$$

$$2.303\log\frac{x_0}{x} =$$

$$k_2\int\left[(H^+) - K\frac{(a-x)(b-x)}{x}\frac{(H^+)^2}{(K_A + (H^+))(K'_B + (H^+))}\right]dt. \quad (VII_2)$$

Now from (IVa), (IVb), (Va), (Vb), since in the absence of other electrolytes

$$(H^+) = (CH_3COO^-) - (C_6H_5NH_3^+), \quad (VIII)$$

$$(H^+) = \frac{K_A}{2}\left(\sqrt{1 + \left(\frac{4K'_B}{K_A} - 2\right)\frac{a-x}{b-x+K'_B+(H^+)} + \left(\frac{a-x}{b-x+K'_B+(H^+)}\right)^2} + \frac{a-x}{b-x+K'_B+(H^+)} - 1\right) \quad (IX)$$

whence (H^+) may be calculated by approximation. Then by plotting, respectively, $\log\left(\frac{b-x}{a-x}\right)$ and $-\log x$ against the "effective" values for the time, obtained by multiplying every measured time interval by the mean value of the respective expression in square brackets, straight lines should

be obtained from whose slopes, m_1, m_2, the reaction velocity constants can be calculated, as in the earlier case of hydrolysis by hydrochloric acid, by means of the equations

$$k_1 = \frac{2.303\ m_1}{b - a} \qquad k_2 = 2.303\ m_2. \qquad\qquad (X)$$

The results are shown plotted in Figs. 3 and 4; the data and calculations will be found in Tables 4, 5 and 6. The concordance is not all that could be desired, but since the equilibrium experiments indicated side

TABLE 4.

Series No.	Time. Hrs.	x mol/l.	Log $(a—x)/(b—x)$.	$10^4(H^+)$ mol/l.	Factor. [ ].	$\Delta t\times[\ ]_{mean}$. Hrs.	t'. Hrs.
6–2	6.5	0.01476	0.720	1.598	0.312		...
						3.56	
3	18.0	0.02970	0.739	1.646	0.309		3.56
						3.21	
4	28.5	0.04877	0.768	1.712	0.302		6.77
						6.04	
5	48.75	0.06955	0.801	1.798	0.293		12.81
						6.60	
6	72.0	0.0899	0.836	1.895	0.276		19.41
						6.88	
7	98.0	0.1107	0.879	2.018	0.254		26.29
5–1	1.92	0.00329	0.530	1.221	0.2579		...
						1.42	
2	7.42	0.00776	0.535	1.229	0.2575		1.42
						2.93	
3	18.92	0.02061	0.550	1.255	0.2528		4.35
						2.63	
4	29.42	0.02990	0.560	1.274	0.2490		6.98
						4.99	
5	49.67	0.04432	0.580	1.309	0.2444		11.97
						5.60	
6	72.92	0.0580	0.598	1.343	0.2370		17.57
						6.04	
7	98.92	0.0717	0.618	1.384	0.2274		23.61
10–1	26	0.01778	0.386	0.998	0.2086		...
						4.36	
2	47	0.02381	0.392	1.006	0.2059		4.36
						9.98	
3	97	0.04504	0.414	1.037	0.1933		14.34
						17.41	
4	193	0.0729	0.446	1.086	0.1696		31.75
						24.89	
5	361	0.1027	0.490	1.153	0.1266		56.64
						32.58	
6	697	0.1265	0.531	1.222	0.0673		89.22

TABLE 5.

Series No.	Time. Hours.	x mol/l.	$1 + \log x$.	$10^4(\mathrm{H}^+)$ mol/l.	$10^4[\ ]$ mol/l.	$10^4 \Delta t \times [\ ]_{\text{mean}}$ mol $\times$ hr./l.	$10^4 t'$ mol $\times$ hr./l.
9–1	46.5	0.2321	0.3657	4.188	3.902		...
						86.1	
2	70.5	0.2189	0.3402	3.604	3.268		86.1
						143.7	
3	118.5	0.2022	0.3058	3.110	2.716		229.8
						121.2	
4	164.5	0.1956	0.2914	2.968	2.552		351.0
						181.5	
5	238.5	0.1867	0.2711	2.800	2.354		532.5
8–1	47	0.2407	0.3815	3.246	3.105		...
						68.1	
2	71	0.2267	0.3554	2.746	2.573		68.1
						113.3	
3	119	0.2092	0.3206	2.359	2.151		181.4
						93.6	
4	165	0.1958	0.2918	2.150	1.916		275.0
						92.3	
5	215	0.1860	0.2695	2.030	1.776		367.3
7–1	49	0.2546	0.4059	2.821	2.763		...
						58.6	
2	73	0.2373	0.3753	2.196	2.117		58.6
						100.1	
3	125	0.2181	0.3387	1.832	1.730		158.7
						68.6	
4	167	0.2039	0.3094	1.662	1.543		227.3
						109.3	
5	241	0.1912	0.2815	1.547	1.414		336.6

TABLE 6.

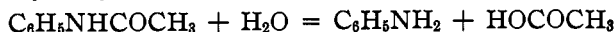| Series No.	$\Sigma \mathrm{CH_3CO_2H}$ a mol/l.	$\Sigma \mathrm{C_6H_5NH_2}$ b mol/l.	Slope m recip. hr.	$2.303 m/a-b$ k_1 1/mol $\times$ hr.	k_2 1/mol $\times$ hr.	K.
6	1.437	0.2860	0.00604	0.01209		
5	0.963	0.2862	0.00374	0.01272		
10	0.672	0.2870	0.001974	0.01180		
			1/mol $\times$ hr.			
9	1.429	0.2860	2.65		6.10	
8	0.954	0.2862	3.09		7.12	
7	0.670	0.2870	3.65		8.41	
15	1.442	0.2860				7.92 $\times$ 10^{-4}
14	0.963	0.2862				8.78 $\times$ 10^{-4}
13	0.671	0.2870				9.32 $\times$ 10^{-4}
Extrapolated to 0 conc. of $\mathrm{CH_3CO_2H}$						10.54 $\times$ 10^{-4}

reactions[1]—such as the formation of diphenylamine (which was in fact shown qualitatively to be formed)—a high degree of concordance could hardly be expected. There is the possibility that in addition to the

[1] All the tubes used in the quantitative work developed a more or less pronounced magenta color, even though they were exhausted down to 25 mm. before sealing. Subse-

catalytic hydrolysis of acetanilide by hydrogen ion and by hydroxyl ion

$$C_6H_5NHCOCH_3 + H^+ + H_2O = C_6H_5NH_3^+ + HOCOCH_3$$

$$C_6H_5NHCOCH_3 + OH^- = C_6H_5NH_2 + OCOCH_3^-$$
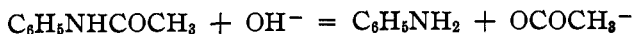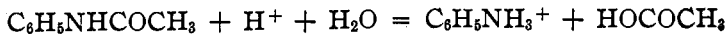
direct hydrolysis by water may occur

$$C_6H_5NHCOCH_3 + H_2O = C_6H_5NH_2 + HOCOCH_3$$

at a rate which is negligible in solutions containing an appreciable amount of strong acid or alkali and yet large enough to constitute the greater part of the hydrolysis in neutral solution.
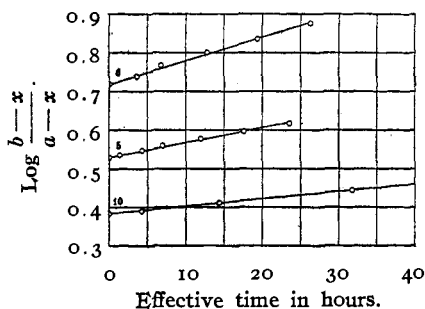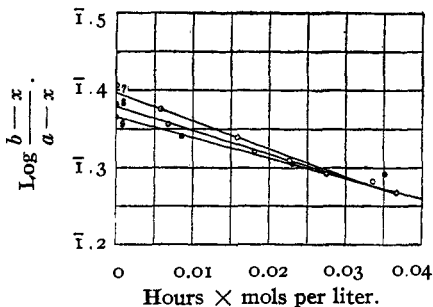

Fig. 3.

Fig. 4.

The results of the experiments on the hydrolysis in the presence of hydrochloric acid agree within the constancy of the temperature, about $0.2°$, corresponding to 2% on the value of k_2, so that the mean value, reduced to $100°$, may be taken as 8.4 ± 0.1. This result is to be compared with the corresponding constant found by Davis[1] for the hydrolysis by alkali, namely 3.2 (at the boiling point of tenth molal solution). The most probable value of the acetylation constant k_1 may be found by extrapolating[2] the equilibrium constant K to zero concentration of acetic acid, and multiplying by k_2. The values thus obtained are $K = 10.5 \times 10^{-4}$, $k_1 = 0.89 \times 10^{-2}$.

Summary.

1. The hydrolysis of acetanilide by hydrochloric acid proceeds in accordance with the equation

$$C_6H_5NHCOCH_3 + H^+ + H_2O = C_6H_5NH_3^+ + HOCOCH_3.$$
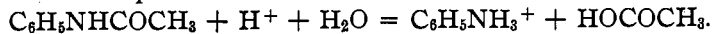
2. The velocity constant at $100°$ for the hydrolysis of acetanilide by hydrochloric acid is 8.4 ± 0.1 liters[3] per mol per hour. (Davis found 3.2 for hydrolysis by alkali.)

quent experiment has shown that *continued* boiling out under this pressure entirely prevents the development of color, but to do so without change in concentration seemed impracticable.

[1] Davis, *Loc. cit.* Both constants are in liters per mol per hour.

[2] Direct extrapolation of the values of k_1 gives a result consistent with this, but the curvature of the graph makes extrapolation inconclusive.

[3] Concentrations are stated in mols per cubic decimeters at $100°$.

3. The most probable value (obtained by extrapolation to zero concentration of acetic acid) of the equilibrium constant (omitting the concentration of the water) for the reaction as written above is 950 (= $1/10.5 \times 10^{-4}$); this corresponds to a velocity constant for the acetylation of 0.0089 liters per mol per hour.

In conclusion we wish to express our gratitude to Prof. H. C. Biddle for his many helpful suggestions.

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THE ATOMIC WEIGHT OF ZIRCONIUM.

BY FRANCIS P. VENABLE AND JAMES M. BELL.

As the results of our work involve a considerable change in the atomic weight of zirconium, it is well to give a brief review of the previous determinations of this constant.

TABLE I.[1]
Previous Determinations of the Atomic Weight of Zirconium.

	Date.	Chemist.	Ratio.	Number of analyses.	Atomic weight.
1...............	1825	Berzelius[2]	$Zr(SO_4)_2:ZrO_2$	6	89.46
2............	1881	Weibull[3]	$Zr(SO_4)_2:ZrO_2$	7	89.54
3............	1889	Bailey[4]	$Zr(SO_4)_2:ZrO_2$	8	90.65
4............	1881	Weibull[3]	$Zr(SeO_4)_2:ZrO_2$	5	90.79
5............	1860	Marignac[5]	$K_2ZrF_6:K_2SO_4$	4	90.03
6............	1860	Marignac[5]	$K_2ZrF_6:ZrO_2$	4	91.54
7............	1898	Venable[6]	$ZrOCl_2.3H_2O:ZrO_2$	10	90.81
8............	1844	Hermann[7]	$ZrCl_4:?$	1	88.64
9............	1844	Hermann[7]	$2ZrOCl_2.9H_2O:?$	2	89.98

We believe that little dependence is to be placed upon any of these figures. In the first three, zirconium sulfate is used. It is now well known that this substance cannot be freed from water without losing some sulfur trioxide. In addition it is difficult to prepare pure, especially avoiding the products of hydrolysis.

The series of determinations in No. 7 was carried out by one of us in 1898 and at the time of publication several sources of error were pointed out and a promise given of further work on the subject. Circumstances have prevented the fulfillment of the promise until now. The most serious

[1] Clark. "Constants of Nature." p. 287 (1910).
[2] *Ann. Physik.*, [1] 4, 126 (1825).
[3] *Lund. Arsschrift.* 18 (1881–2).
[4] *Chem. News,* 60, 6, 17, 32 (1889).
[5] *Ann. chim. phys.*, [3] 60, 270 (1860).
[6] THIS JOURNAL, 20, 119 (1898).
[7] *J. prakt. Chem.*, 31, 75 (1844).