# Heats of Aminolysis and Hydrolysis of Some N-Acetyl Compounds and of Acetic Anhydride

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Enthalphy changes for some aminolysis and hydrolysis reactions involving acetyl compounds have been determined calorimetrically. For the idealized, isothermal (25°C) reaction

$$RNAc(s) + R'NH_2(l) \to RNH(s) + R'NHAc(l/s)$$
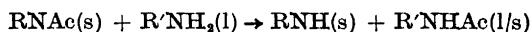
$\Delta H°$ was found to be
-18.07 ± 0.08 kcal/mole for RNH = imidazole and
$R'NH_2$ = butylamine
-20.50 ± 0.06   »   » RNH = 1,2,4-triazole and
$R'NH_2$ = butylamine
-17.28 ± 0.08   »   » RNH = 1,2,4-triazole and
$R'NH_2$ = aniline
-20.22 ± 0.08   »   » RNH = tetrazole and
$R'NH_2$ = aniline

For the reaction
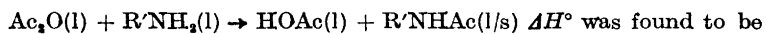
$Ac_2O(l) + R'NH_2(l) \to HOAc(l) + R'NHAc(l/s)$ $\Delta H°$ was found to be
-27.06 ± 0.11 kcal/mole for $R'NH_2$ = butylamine
-24.11 ± 0.06   »   »   »   = aniline

The standard heat of hydrolysis of acetic anhydride has been determined to be -14.00 ± 0.09 kcal/mole. From the obtained data the standard heats of hydrolysis of butyl acetamide and acetanilide have been derived, as well as the heat of combustion of acetanilide.

In a recent paper [1] heats of hydrolysis of N-acetylated imidazole, 1,2,4-triazole and tetrazole were reported. The thermochemical investigation of these compounds has now been extended to include aminolysis reactions with butylamine and aniline. In order to compare the heats of hydrolysis data with those obtained from the aminolysis experiments, the heats of hydrolysis of butyl acetamide and acetanilide must be known. These amides are not easily hydrolyzed at 25°C, but their heats of hydrolysis can be obtained by combining the values of the heat of hydrolysis of acetic anhydride and the heats of amino-

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lysis of acetic anhydride by butylamine and aniline. The heat of hydrolysis of acetic anhydride is known from the work by Kistiakowsky and co-workers [2]. However, as this value is of prime importance in calorimetry of aminolysis reactions, it has been redetermined in this work.

EXPERIMENTAL

Materials. Imidazole, 1,2,4-triazole, tetrazole, and the corresponding N-acetyl compounds were described in Ref.[1]

Acetic anhydride (Merck, analytical grade) was fractionally distilled through a 25-plate column at atmosphere pressure. A fraction constantly boiling at 139.3°C (754 mm Hg) was collected. Potentiometric titration with sodium hydroxide and gas chromatographic analysis (Pye Argon chromatograph) indicated 99.9 % purity.

Aniline of analytical grade was heated at 100°C with KOH pellets for 2 h, followed by distillation under reduced pressure through a 10-plate column. $n_D^{25} = 1.5838$; $d_4^{25} = 1.0171$.

Acetanilide was prepared from aniline and acetic anhydride and the product obtained was recrystallized from ethanol. Mp. 114.0 − 114.4°C.

Acetic acid (Merck, analytical grade) was purified by freezing out four times. Titration with NaOH indicated 100.0 % purity.

Butylamine of a *purum* grade was dried by refluxing it with KOH pellets for 2 h followed by fractionation at atmosphere pressure in a 25-plate column. Potentiometric titration with standard hydrochloric acid gave an equivalent weight corresponding to 100.0 % purity.

Butyl acetamide was prepared from butylamine and acetic anhydride [3] and fractionally distilled. $n_D^{25} = 1.4389$; $d_4^{25} = 0.8953$.

Benzene of a *purum* quality, free from thiophene, was dried by phosphorus pentoxide and then distilled through a 25-plate column.

Apparatus. The reactions were carried out in an "isothermal-jacket" calorimeter, which has been described in detail elsewhere (Type D in Ref.[4]).

Calibration. The heat equivalent of the calorimeter, including contents, was determined electrically by passing a known current for a given time (300 sec. except for the system with aniline where it was 300 − 900 sec.) through the heating element. The calibrations were performed on the system after the reaction had taken place. No significant correlation between the amount and kind of reactant and the obtained heat capacity values was observed, and therefore mean values of the obtained heat capacities have been used in calculating the results.

Calorimetric procedure. The calorimeter was charged with 100 ml of liquid. Heats of aminolysis and hydrolysis measurements were supplemented by determination of heats of solution in order to obtain the standard enthalphy change, $\Delta H°$, of the reaction.

All reactions investigated were very rapid (< 2 min) except for the aminolysis of the acetylated heterocycles by aniline. Attempts to determine the heat of reaction between aniline and N-acetyl imidazole with the apparatus used in this work failed, as the reaction was too slow. For the reactions between aniline and the acetylated triazole and tetrazole reaction periods had to be taken as long as 20 to 30 min. Thermal leakage in these cases, as well as in the solution experiments with triazole and tetrazole in aniline, was calculated by the Regnault-Pfaundler method [5]. In all other cases the initial and final thermistor resistance values were evaluated graphically.

When butylamine and its mixture with benzene were used as calorimetric liquids small corrections were applied to account for evaporation during the breaking of the ampoule.

The aminolysis reactions were carried out in the pure amines except for the case of acetic anhydride in butylamine, where the reaction was found to be too vigorous and was therefore performed in butylamine-benzene (1:10 parts by volume) solution.

Units of measurements. The results of the calorimetric experiments are expressed in terms of the defined calorie, equal to 4.1840 abs. joules, and refer to the isothermal process at 25°C, and to the true mass.
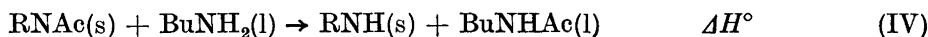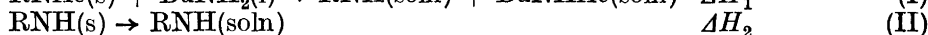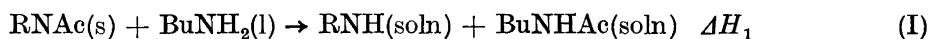
RESULTS

Aminolysis in pure butylamine

Results from the determination of heats of aminolysis of N-acetyl imidazole and N-acetyl 1,2,4-triazole are given in Table 1. log R_i/R_f is the expression proportional to the temperature change; R_i and R_f are the corrected thermistor resistance values at the start and the end, respectively, of the main period. From four calibration experiments the mean heat equivalent was calculated to be 4 741 + 5 * cal/unit of log R_i/R_f.

Results from determination of heats of solution in butylamine are given in Table 2.

Correction to the standard state. The idealized, isothermal reaction IV is obtained from eqns. I to III.

$$RNAc(s) + BuNH_2(l) \rightarrow RNH(soln) + BuNHAc(soln) \quad \varDelta H_1 \quad \text{(I)}$$
$$RNH(s) \rightarrow RNH(soln) \quad \varDelta H_2 \quad \text{(II)}$$
$$BuNHAc(l) \rightarrow BuNHAc(soln) \quad \varDelta H_3 \quad \text{(III)}$$

$$RNAc(s) + BuNH_2(l) \rightarrow RNH(s) + BuNHAc(l) \quad \varDelta H° \quad \text{(IV)}$$
$$\varDelta H° = \varDelta H_1 - \varDelta H_2 - \varDelta H_3$$

For RNH = Imidazole $\varDelta H° = -18.07 \pm 0.06$ and
for RNH = 1,2,4-Triazole $\varDelta H° = -20.50 \pm 0.04$ kcal/mole
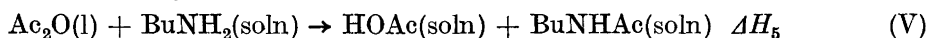
Taking into consideration possible systematic errors in the analysis and in heat equivalent values, the standard enthalphy change for the reaction with butylamine was found to be -18.07 ± 0.08 and -20.50 ± 0.06 kcal/mole for N-acetyl imidazole and N-acetyl 1,2,4-triazole, respectively.

Aminolysis in butylamine-benzene

From six calibration experiments the mean heat equivalent was calculated to be 4 012 $\pm$ 2 cal/unit of log R_i/R_f.

Results from the determination of heat of aminolysis of acetic anhydride are given in Table 3. Results from heats of solution measurements in butyl-amine-benzene are given in Table 4.

Correction to the standard state. The idealized isothermal reaction IX is obtained from eqns. V to VIII.

$$Ac_2O(l) + BuNH_2(soln) \rightarrow HOAc(soln) + BuNHAc(soln) \quad \varDelta H_5 \quad \text{(V)}$$
$$BuNHAc(l) \rightarrow BuNHAc(soln) \quad \varDelta H_6 \quad \text{(VI)}$$
$$HOAc(l) \rightarrow HOAc(soln) \quad \varDelta H_7 \quad \text{(VII)}$$
$$BuNH_2(l) \rightarrow BuNH_2)soln) \quad \varDelta H_8 \quad \text{(VIII)}$$

$$Ac_2O(l) + BuNH_2(l) \rightarrow HOAc(l) + BuNHAc(l) \quad \varDelta H° \quad \text{(IX)}$$
$$\varDelta H° = \varDelta H_5 - \varDelta H_6 - \varDelta H_7 + \varDelta H_8$$
$$\varDelta H° = -27.06 \pm 0.08 \text{ kcal/mole}$$

* When five or more determinations are performed, the uncertainties are given as the standard deviation of the mean. Otherwise they are the average deviation of the mean.
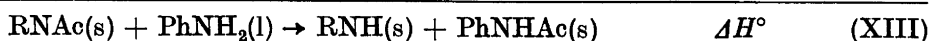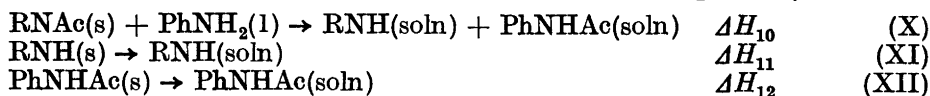
When systematic errors are considered, this value of ΔH° is -27.06 ± 0.11 kcal/mole.

Aminolysis in aniline

From eight calibration experiments the mean heat equivalent was calculated to be 5066 ± 4 cal/unit of log R_i/R_f.

Results from the determination of heats of aminolysis in aniline are given in Table 5 and results from heats of solution in aniline are given in Table 6.

Corrections to the standard states. The idealized isothermal reactions XIII and XVI are obtained from eqns. X to XII and XIV to XII, respectively.

$$\text{RNAc(s)} + \text{PhNH}_2(\text{l}) \rightarrow \text{RNH(soln)} + \text{PhNHAc(soln)} \qquad \Delta H_{10} \qquad \text{(X)}$$
$$\text{RNH(s)} \rightarrow \text{RNH(soln)} \qquad \Delta H_{11} \qquad \text{(XI)}$$
$$\text{PhNHAc(s)} \rightarrow \text{PhNHAc(soln)} \qquad \Delta H_{12} \qquad \text{(XII)}$$

$$\text{RNAc(s)} + \text{PhNH}_2(\text{l}) \rightarrow \text{RNH(s)} + \text{PhNHAc(s)} \qquad \Delta H^\circ \qquad \text{(XIII)}$$
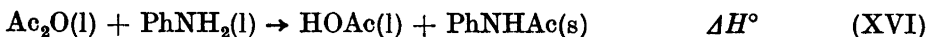$$\Delta H^\circ = \Delta H_{10} - \Delta H_{11} - \Delta H_{12}$$

For RNH = 1,2,4-triazole $\Delta H^\circ = -17.28 \pm 0.07$ and
for RNH = tetrazole $\quad \Delta H^\circ = -20.22 \pm 0.07$ kcal/mole

After systematic errors have been considered, the standard enthalphy change for the reaction with aniline is -17.28 ± 0.08 and -20.22 ± 0.08 kcal/mole for N-acetyl 1,2,4-triazole and N-acetyl tetrazole, respectively.

$$\text{Ac}_2\text{O}(\text{l}) + \text{PhNH}_2(\text{l}) \rightarrow \text{HOAc(soln)} + \text{PhNHAc(soln)} \qquad \Delta H_{14} \qquad \text{(XIV)}$$
$$\text{HOAc(l)} \rightarrow \text{HOAc(soln)} \qquad \Delta H_{15} \qquad \text{(XV)}$$
$$\text{PhNHAc(s)} \rightarrow \text{PhNHAc(soln)} \qquad \Delta H_{12} \qquad \text{(XII)}$$

$$\text{Ac}_2\text{O}(\text{l}) + \text{PhNH}_2(\text{l}) \rightarrow \text{HOAc(l)} + \text{PhNHAc(s)} \qquad \Delta H^\circ \qquad \text{(XVI)}$$
$$\Delta H^\circ = \Delta H_{14} - \Delta H_{15} - \Delta H_{12}$$
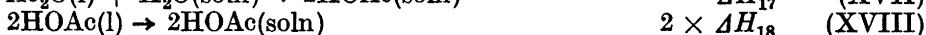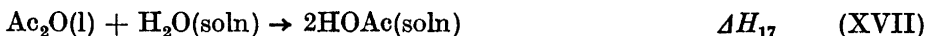$$\Delta H^\circ = -24.11 - 0.05 \text{ kcal/mole}$$

When allowances are made for possible systematic errors, this value is $\Delta H^\circ = -24.11 \pm 0.06$ kcal/mole.

Hydrolysis of acetic anhydride

The hydrolysis of acetic anhydride was carried out in 0.8 N aqueous solution of sodium hydroxide (in connection with other hydrolysis measurements [1]). The obtained mean heat equivalent of the system was 9071 ± 5 cal/unit of log R_i/R_f.

Results from the heat of hydrolysis measurements are given in Table 7.

Correction to the standard state. The idealized isothermal reaction XX was obtained from eqns. XVII to XIX. ΔH_{18} and ΔH_{19} were found to be -13.64 and -0.02 kcal/mole, respectively [1].

$$\text{Ac}_2\text{O}(\text{l}) + \text{H}_2\text{O(soln)} \rightarrow 2\text{HOAc(soln)} \qquad \Delta H_{17} \qquad \text{(XVII)}$$
$$2\text{HOAc(l)} \rightarrow 2\text{HOAc(soln)} \qquad 2 \times \Delta H_{18} \qquad \text{(XVIII)}$$
$$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(soln)} \qquad \Delta H_{19} \qquad \text{(XIX)}$$

$$\text{Ac}_2\text{O}(\text{l}) + \text{H}_2\text{O(l)} \rightarrow 2\text{HOAc(l)} \qquad \Delta H^\circ \qquad \text{(XX)}$$
$$\Delta H^\circ = \Delta H_{17} - 2 \times \Delta H_{18} + \Delta H_{19}$$
$$\Delta H^\circ = -14.00 \pm 0.05 \text{ kcal/mole}$$

After making allowance for systematic errors, $\Delta H°$ was found to be -14.00 ± 0.09 kcal/mole. This value is in fair agreement with that by Kistiakowsky *et al.*[2], -13.92 kcal/mole *. In the following -13.96 ± 0.06 kcal/mole will be used, being the mean between the two determinations.

Table 1. Heats of aminolysis in butylamine

Substance	mmoles	$10^4 \cdot \log R_i/R_f$	$-\Delta H$, kcal/mole
N-acetyl imidazole	1.886	74.85	18.82
	1.888	75.18	18.88
	2.044	81.17	18.83
	2.203	87.00	18.72
		Mean	18.81 $\pm$ 0.05
N-acetyl 1,2,4-triazole	2.128	102.28	22.79
	2.872	137.96	22.77
	2.799	134.20	22.73
	2.104	101.16	22.79
		Mean	22.77 $\pm$ 0.02

Table 2. Heats of solution in butylamine

Substance	mmoles	$10^4 \cdot \log R_i/R_f$	$-\Delta H$, kcal/mole
Imidazole	2.319	-2.83	-0.58
	2.871	-3.61	-0.60
	2.500	-3.02	-0.57
		Mean	-0.58 ± 0.01
1,2,4-Triazole	2.530	5.06	0.95
	2.127	4.23	0.94
	2.261	4.52	0.95
		Mean	0.95 $\pm$ 0.01
Butyl acetamide	2.222	6.28	1.34
	2.401	6.52	1.29
	1.898	5.33	1.33
		Mean	1.32 $\pm$ 0.02

Table 3. Heat of aminolysis in butylamine-benzene

Substance	mmoles	$10^4 \cdot \log R_i/R_f$	$-\Delta H$, kcal/mole
Acetic anhydride	1.386	135.45	39.21
	1.374	134.50	39.27
	1.489	146.16	39.38
	1.270	124.61	39.37
		Mean	39.31 $\pm$ 0.07

* The value is corrected to 25°C; the measurements were performed at 30°C. Uncertainties were not reported.

Table 4. Heats of solution in butylamine-benzene.

Substance	mmoles	$10^4 \cdot \log R_i/R_f$	$-\Delta H$, kcal/mole
Butyl acetamide	1.273	−4.47	−1.41
	1.211	−4.36	−1.44
	1.436	−5.20	−1.45
			Mean −1.43 ± 0.02
Acetic acid	1.269	41.99	13.28
	1.197	39.13	13.12
	1.345	44.47	13.26
	1.206	40.15	13.36
	1.129	37.49	13.32
	1.293	42.76	13.27
			Mean 13.27 ± 0.03
Butylamine	1.165	−1.11	−0.38
	1.040	−1.05	−0.41
	1.045	−1.16	−0.45
			Mean −0.41 ± 0.02

Table 5. Heats of aminolysis in aniline.

Substance	mmoles	$10^4 \cdot \log R_i/R_f$	$-\Delta H$, kcal/mole
N-Acetyl 1,2,4-triazole	3.383	71.91	10.77
	3.003	63.26	10.67
	2.489	53.46	10.88
			Mean 10.77 ± 0.07
N-Acetyl tetrazole	1.621	48.01	15.00
	2.134	63.21	15.01
	1.890	55.68	14.92
			Mean 14.98 ± 0.04
Acetic anhydride	3.056	129.59	21.48
	2.996	128.04	21.65
	2.925	124.99	21.65
	2.831	120.96	21.65
	2.996	128.54	21.73
			Mean 21.63 ± 0.04

Heats of hydrolysis of butyl acetamide and acetanilide

By comparing standard heats of hydrolysis for the heterocyclic acetates and acetic anhydride with the corresponding aminolysis data, it is possible to derive accurate values for the heats of hydrolysis of butyl acetamide and acetanilide, and to check the calorimetric results given in Ref.[1] and those arrived at here.

From the reaction schemes given below three independent values for respective heats of hydrolysis are derived.

Table 6. Heats of solution in aniline

Substance	mmoles	$10^4 \cdot \log R_i/R_f$	$-\Delta H$ kcal/mole
1,2,4-Triazole	2.857	−14.47	−2.57
	2.926	−14.69	−2.54
	2.879	−14.57	−2.56
		Mean	−2.56 ± 0.01
Tetrazole	2.223	− 5.35	−1.22
	1.871	− 5.05	−1.37
	2.405	− 5.99	−1.26
	2.483	− 6.36	−1.30
		Mean	−1.29 ± 0.05
Acetanilide	3.145	−24.49	−3.94
	2.918	−22.65	−3.93
	2.961	−23.18	−3.97
	3.036	−23.73	−3.96
		Mean	−3.95 ± 0.02
Acetic acid	3.016	8.75	1.47
	3.024	8.61	1.44
	3.281	9.64	1.49
	3.346	9.68	1.47
		Mean	1.47 ± 0.01

Table 7. Heat of hydrolysis of acetic anhydride.

Substance	mmoles	$10^4 \cdot \log R_i/R_f$	$-\Delta H$ kcal/mole
Acetic anhydride	1.665	75.91	41.36
	1.874	85.21	41.25
	1.539	69.94	41.22
	1.561	71.04	41.28
	1.512	68.82	41.29
	1.443	65.45	41.14
		Mean	41.26 ± 0.03

		$-\Delta H°$, kcal/mole
A	N-acetyl imidazole(s) + H_2O(l) → imidazole(s) + HOAc(l)	4.83 ± 0.05
	N-acetyl imidazole(s) + $BuNH_2$(l) → imidazole(s) + BuNHAc(l)	18.07 ± 0.08
	BuNHAc(l) + H_2O(l) → HOAc(l) + $BuNH_2$(l)	−13.24 ± 0.09
B	N-acetyl triazole(s) + H_2O(l) → triazole(s) + HOAc(l)	7.29 ± 0.06
	N-acetyl triazole(s) + $BuNH_2$(l) → triazole(s) + BuNHAc(l)	20.50 ± 0.06
	BuNHAc(l) + H_2O(l) → HOAc(l) + $BuNH_2$(l)	−13.21 ± 0.08
C	Ac_2O(l) + H_2O(l) → 2 HOAc(l)	13.96 ± 0.06
	$BuNH_2$(l) + Ac_2O(l) → BuNHAc(l) + HOAc(l)	27.06 ± 0.11
	BuNHAc(l) + H_2O(l) → HOAc(l) + $BuNH_2$(l),	−13.10 ± 0.12

An earlier value, −12.73 ± 0.10 kcal/mole [3], for the heat of the hydrolysis of butyl acetamide derived from measurements according to route C is within twice the sum of

the combined uncertainties and therefore indistinguishable from the value now reported. However, the present experiments were performed with reagents of higher purity and in a more suitable calorimetric system, so that the previous value will not be considered. The heat of hydrolysis of butyl acetamide is given as $+ 13.20 \pm 0.05$ kcal/mole, being a weighed mean [6] of the results derived from routes A to C.

		$-\Delta H°$, kcal/mole
D	N-acetyl triazole(s) + H$_2$O(l) → triazole(s) + HOAc(l)	7.29 ± 0.06
	N-acetyl triazole(s) + PhNH$_2$(l) → triazole(s) + PhNHAc(s)	17.28 ± 0.08
	PhNHAc(s) + H$_2$O(l) → PhNH$_2$(l) + HOAc(l)	$- 9.99 \pm 0.10$
E	N-acetyl tetrazole(s) + H$_2$O(l) → tetrazole(s) + HOAc(l)	10.31 ± 0.09
	N-acetyl tetrazole(s) + PhNH$_2$(l) → tetrazole(s) + PhNHAc(s)	20.22 ± 0.08
	PhNHAc(s) + H$_2$O(l) → PhNH$_2$(l) + HOAc(l)	$- 9.91 \pm 0.12$
F	Ac$_2$O(l) + H$_2$O(l) → 2HOAc(l)	13.96 ± 0.06
	Ac$_2$O(l) + PhNH$_2$(l) → PhNHAc(s) + HOAc(l)	24.11 ± 0.06
	PhNHAc(s) + H$_2$O(l) → PhNH$_2$(l) + HOAc(l)	-10.15 ± 0.08

The heat of hydrolysis of acetanilide is taken as $+ 10.05 \pm 0.06$ kcal/mole, *i.e.*, the weighed mean of the results derived from routes D to F.

Comparison with heats of combustion data

Heats of combustion of acetanilide, aniline, and acetic acid are known and can therefore be checked by the present reaction calorimetric data.

For aniline(l) and acetic acid(l) modern data give the heats of combustion as -810.5[7] and -209.0[8] kcal/mole, respectively.

For acetanilide no recent determinations have been made. The value by Stohmann and Schmidt, as corrected in Kharasch's compilation [9], is -1010.4 kcal/mole. The derived enthalpy change for the standard hydrolysis reaction thus becomes $+ 9.1$ kcal/mole or 0.9 kcal/mole too low in comparison with the data given here. Assuming the data for aniline and acetic acid to be correct, the heat of combustion of acetanilide should be -1009.5 kcal/mole.

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