

Some Thermochemical Properties of *N,N,N*-Triacetylammonia

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The enthalpy increment ΔH° (25°) for the isothermal, standard state hydrolysis reaction



has been determined calorimetrically: $\Delta H^\circ = -24.74 \pm 0.02$ kcal/mole. Conversion to the ideal gaseous state yields $\Delta H_{\text{gas}}^\circ = -16.0 \pm 0.3$ kcal/mole. From these data the standard heat of formation of *N,N,N*-triacetylammonia has been derived: $\Delta H_f^\circ = -146.6$ kcal/mole. Some correlations are made between the thermochemical properties of triacetylammonia and those of the structurally related molecules, mono and diacetylammonia.

The heats of hydrolysis of several *N* substituted amides have been determined recently.¹⁻³ In the present paper some thermochemical data for *N,N,N*-triacetylammonia is reported. The two-stage aqueous hydrolysis of the compound is a well-defined, rapid and quantitative process and is thus well suited to a thermochemical investigation.

EXPERIMENTAL

Materials. *N,N,N*-Triacetylammonia was prepared by acetylation of *N,N*-diacetylammonia using an acetone solution of ketene as acetylating agent.⁴ The reaction product was rapidly fractionated under 12 mm Hg pressure using a simple column. It was further purified by fractional distillation (12 mm Hg) followed by fractional crystallisation (3 times) at +5°, and finally treated with Drierite and distilled. The equivalent weight was determined by alkaline hydrolysis followed by back titration with standard hydrochloric acid: calc. 143.14; found 143.07. $n_D^{25} = 1.4466$; $d^{25} = 1.1280$. (*N,N,N*-Triacetylammonia has previously been described erroneously as a solid, m.p. 77–79°.^{5,6} This compound was probably *N,N*-diacetylammonia, m.p. 81°.)

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The NMR spectrum of triacetylammnia in CHCl_3 solution showed only one peak ($\tau=2.37$ ppm) in agreement with the assumed structure in which all the nine hydrogen atoms are equivalent.

In the calorimetric experiments *N,N,N*-triacetylammnia was hydrolysed in 0.8 N sodium hydroxide, water-ethanol solution (160 g NaOH, 2 l water, 3 l 96 % ethanol).

Reaction calorimetry. All thermochemical measurements were performed using an LKB Precision Calorimeter (constant temperature environment type). The 100 ml glass reaction vessel was charged with the prepared alkaline hydrolysis solution and the pure liquid triacetylammnia was stored under nitrogen in the sealed glass ampoule. The heat equivalent of the calorimeter plus contents was determined by passing a known constant current (100 mA) for a specified time interval (600 sec) through the 50 ohm calibration heater. Such electrical calibration experiments were performed both before and after the hydrolysis reaction.

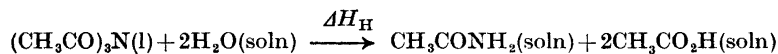
Vaporisation calorimetry. The heat of vaporisation of triacetylammnia was determined calorimetrically at 25.00° by the method described previously.⁷

Units. All enthalpy data are expressed in terms of the defined calorie = 4.1840 abs. joules and is referred to the isothermal process at 25.00° .

RESULTS

Reaction calorimetric measurements. The experimental results are summarized in Table 1. ϵ_b and ϵ_a are the heat equivalents of the calorimetric

Table 1.



Calibration		Hydrolysis reaction			
ϵ_b	ϵ_a	$(\text{CH}_3\text{CO})_3\text{N}$ mmoles	R_i (ohms)	R_f (ohms)	$-\Delta H_{\text{H}}$ kcal/mole
2180.4	2178.2	1.833	2094.38	2017.69	44.34
2180.6	2178.8	1.859	2094.49	2016.74	44.35
2181.7	2176.2	1.899	2094.54	2015.09	44.37
2181.8	2173.4	1.816	2094.57	2018.44	44.40
2181.3	2175.2	1.871	2094.44	2016.40	44.20

$$\Delta H_{\text{H}} = -44.33 \pm 0.02 \text{ kcal/mole.}$$

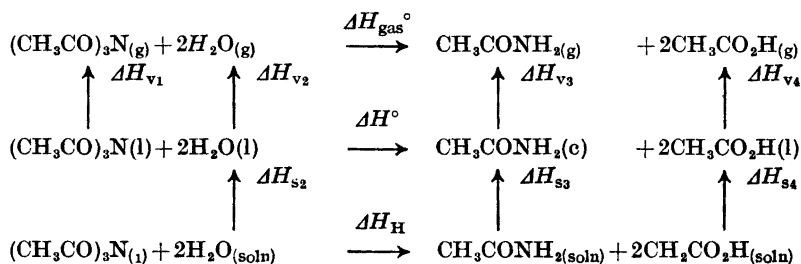
system before and after the initiation of the reaction respectively. $R_i - R_f = \Delta R$ is the corrected thermistor resistance change at the experiment. $\Delta H_{\text{H}}(25.00^\circ)$ was computed from the relationship $\epsilon_m \Delta R / m R_m$ where $\epsilon_m = 0.5(\epsilon_b + \epsilon_a)$ and $R_m = 0.5(R_i + R_f)$, R_m corresponds to 25.00° , m is the sample mass (mmoles). For the exothermic hydrolysis reaction, the temperature-time curve for the reaction period was assumed to be truly exponential (reaction period 3–4 min) and the ΔR value was computed by extrapolating the fore and after linear parts of the calorimetric curve to the time corresponding to 63 % of the heat evolution (Dickinson extrapolation method). Normal and constant K values (K is Newton's cooling constant) were obtained which indicated the

absence of slow secondary reactions. For an electrical calibration, the temperature-time curve during heat input is linear and extrapolations were taken to the time value corresponding to 50 % of the total heat evolution. The uncertainty interval associated with ΔH_{H} is given as the single standard deviation of the mean to which has been added estimated systematic errors.

Heat of vaporisation measurements. The mean heat of vaporisation for triacetylammonia (ΔH_{V1}) derived from four measurements was $+14.44 \pm 0.02$ kcal/mole.

Conversion to the standard state. ΔH° and $\Delta H_{\text{gas}}^\circ$ were evaluated directly from the empirical thermochemical cycle (Scheme A).

SCHEME A



$$\Delta H^\circ = \Delta H_{\text{H}} + 2\Delta H_{\text{S2}} - \Delta H_{\text{S3}} - 2\Delta H_{\text{S4}} \quad (1)$$

$$\Delta H_{\text{gas}}^\circ = \Delta H^\circ - \Delta H_{\text{V1}} - 2\Delta H_{\text{V2}} + \Delta H_{\text{V3}} + 2\Delta H_{\text{V4}} \quad (2)$$

Supplementary enthalpy data (25.0°) kcal/mole.

$$\begin{array}{ll}
 \Delta H_{\text{S2}} = -0.20 \pm 0.01^8 & \Delta H_{\text{S3}} = +3.25 \pm 0.01^3 \\
 \Delta H_{\text{S4}} = -11.63 \pm 0.02^8 & \Delta H_{\text{V2}} = +10.52 \pm 0.00^9 \\
 \Delta H_{\text{V3}} = +19.2 \pm 0.2^3 & \Delta H_{\text{V4}} = +12.49 \pm 0.07^2 \\
 \therefore \Delta H^\circ = -24.74 \pm 0.02 & \Delta H_{\text{gas}}^\circ = -16.0 \pm 0.3 \text{ kcal/mole}
 \end{array}$$

The standard heat of formation (ΔH_f°) of triacetylammonia was calculated from ΔH° : the standard heats of formation of monoacetamide, acetic acid and water were taken as -76.60 ,⁹ -115.70 ,¹⁰ and -68.32 kcal/mole,⁹ respectively. $\Delta H_f^\circ(\text{CH}_3\text{CO})_3\text{N} = -146.6$ kcal/mole.

DISCUSSION

ΔH° and $\Delta H_{\text{gas}}^\circ$ values for mono, di, and triacetylammonia are collected in Table 2.

The excellence of triacetylammonia as an acetylating agent⁴ is manifested in the highly exothermal nature of reaction II. As the number of substituent acetyl groups on the central basic nitrogen atom increases the $\Delta H_{\text{gas}}^\circ$ term becomes more negative which is believed to be partially due to a release of strain energy during the hydrolysis process. Also, a decrease in the resonance

Table 2.

Standard state hydrolysis reaction	ΔH_f° kcal/mole	ΔH° kcal/mole	$\Delta H_{\text{gas}}^\circ$ kcal/mole
I $(\text{CH}_3\text{CO})_2\text{N}_{(l)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{CH}_3\text{CONH}_{2(c)} + 2\text{CH}_3\text{CO}_2\text{H}_{(l)}$	$(\text{CH}_3\text{CO})_2\text{N}$ -146.6 ^a	-24.74 ± 0.02 ^a	-16.0 ± 0.3 ^a
II $(\text{CH}_3\text{CO})_2\text{N}_{(l)} + \text{H}_2\text{O}_{(l)} \rightarrow (\text{CH}_3\text{CO})_2\text{NH}_{(c)} + \text{CH}_3\text{CO}_2\text{H}_{(l)}$	-	-20.41 ± 0.05 ^a	-14.9 ± 0.5 ^a
III $(\text{CH}_3\text{CO})\text{NH}_{(c)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{CH}_3\text{CONH}_{2(c)} + \text{CH}_3\text{CO}_2\text{H}_{(l)}$	$(\text{CH}_3\text{CO})_2\text{NH}$ -119.7 ^a	-4.33 ± 0.05 ^a	-1.1 ± 0.4 ^a
IV $\text{CH}_3\text{CONH}_{2(c)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{NH}_{3(g)} + \text{CH}_3\text{CO}_2\text{H}_{(l)}$	CH_3CONH_2 -76.6 ^a	+18.2 ± 0.3 ^a	+1.4 ± 0.4 ^a

^a Present work.

stabilisation of the N substituted ammonia should be reflected as a negative increment in $\Delta H_{\text{gas}}^{\circ}$.

Comparison between the gaseous heat of formation data given in this paper and the appropriate bond energy terms and atomic heats of formation * will lead to the following resonance energy ** values: acetic acid, 18.8; acetamide, 18; diacetylammonia, 33; and triacetylammonia, 34 kcal/mole, respectively.

The resonance energy of acetamide is thus approximately equal to that of acetic acid and substitution of a second acetyl group on N approximately doubles the resonance energy of the system whereas attachment of a third acetyl group causes no further increase in resonance energy. Scale structural models show that whereas it is possible for two carbonyl groups and the adjacent N atom to be coplanar, thus facilitating electronic delocalisation, the attachment of a third acetyl group destroys coplanarity and hence the delocalisation mechanism is partially inhibited.

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REFERENCES

1. Wadsö, I. *Acta Chem. Scand.* **16** (1962) 471.
2. Wadsö, I. *Acta Chem. Scand.* **16** (1962) 479.
3. Wadsö, I. *Acta Chem. Scand.* **19** (1965) 1079.
4. Kocheshkov, K. A., Skoldinov, A. P. and Smirnova, N. V. *Dokl. Akad. Nauk. SSSR* **84** (1952) 737; *Chem. Abstr.* **47** (1953) 3233a.
5. Wichelhaus, H. *Ber.* **3** (1870) 847.
6. Rakshit, J. N. *J. Chem. Soc.* **103** (1913) 1557.
7. Wadsö, I. *Acta Chem. Scand.* **20** (1966) 536.
8. Wadsö, I. *Acta Chem. Scand.* **14** (1960) 561.
9. Evans, W.H., Jaffe, J., Levine, S., Rossini, F.D. and Wagman, D.D. *Selected Values of Chemical Thermodynamic Properties, Circular 500*, National Bureau of Standards, U.S. Govt. Printing Office, Washington 1952.
10. Evans, F. W. and Skinner, H. A. *Trans. Faraday Soc.* **55** (1959) 260.
11. Cox, J. D. *Tetrahedron* **18** (1962) 1337.

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* The atomic heats of formation of carbon, hydrogen and oxygen were taken as +170.90, +52.09, and +59.54 kcal/g.atom,¹¹ respectively. The bond energy scheme due to Cox¹¹ was employed: C-H=98.3, C-C=93.4, C=O=160.2 kcal. respectively.

** In this context, the term "resonance energy of a compound" refers to the energy difference between the experimental heat of formation and the thermochemical bond energy summation.