

form of flat needles which melted at 156°. This compound is less soluble than the methyl ester of the hydroxy acid. Hydrolysis with potassium hydroxide in methyl alcohol gave the hydroxy acid, m. p. 236°; 26.8 mg. in 2 cc. of chloroform solution gave $\alpha^{20D} -0.25^\circ$, 1-dm. semi-micro tube, $[\alpha]^{20D} -18.7^\circ$.

Anal. Calcd. for $C_{27}H_{42}O_4$: C, 75.30; H, 9.84. Found: C, 75.44; H, 9.85.

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Summary

Dehydroandrosterone and Δ^5 -3-hydroxychol-

enic acid have been prepared from cholesterol by oxidation. This oxidation is possible provided both the double bond and the hydroxyl group in cholesterol are protected against oxidation. This has been accomplished by oxidation of cholesteryl acetate dibromide with chromic acid. A detailed description of the oxidation process has been given. This method of preparation locates definitely the double bond and determines the spatial arrangement of the hydroxyl group in dehydroandrosterone.

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NOTES

Apparent Molal Heat Capacities of Amino Acids and Other Organic Compounds

By JOHN T. EDSALL

The heat capacities of organic substances in aqueous solution have never been extensively studied. Zwicky¹ pointed out that the apparent molal heat capacities of several organic molecules in water were nearly identical with their molal heat capacities in the pure crystalline state, in other words, that the law of the ideal solution is approximately obeyed. For other substances, however, this is far from true.² A survey of the available data in "International Critical Tables," and of the recent data of Zittle and Schmidt³ on amino acids in water, reveals certain relations between chemical structure and apparent molal heat capacity in water which appear worthy of consideration. In Table I are recorded the apparent molal heat capacities (ϕ) in dilute aqueous solution, and the molal heat capacities (C_p) in the pure state, for a number of substances.⁴

(1) Zwicky, *Physik. Z.*, **27**, 271 (1926).

(2) See for instance Bose, *Z. physik. Chem.*, **88**, 585 (1907).

(3) Zittle and Schmidt, *J. Biol. Chem.*, **106**, 161 (1935).

(4) To make all the data comparable, the value of C_p should preferably be given for the pure liquid state. This is impossible for many substances, such as the amino acids which decompose on melting. In general, the value of C_p for any substance is distinctly higher in the liquid state than for the solid at or near the same temperature. This fact should be remembered in considering the data in Table I, but it does not essentially affect the arguments here advanced.

In the three homologous series recorded (alcohols, fatty acids, amino acids) it will be observed that the introduction of a CH_2 group increases ϕ by 20 to 30 calories per mole (see column headed Δ in Table I), while C_p increases by only 5 to 8 calories per mole for each CH_2 group introduced. Thus the presence of a hydrocarbon chain tends to produce a *positive* deviation from the ideal solution law with respect to heat capacity. This trend is approximately indicated by the series of values of $\phi - C_p$ given in the last column of Table I. On the other hand, substances such as glycerol, urea, dextrose and sucrose, which contain many polar groups and no hydrocarbon chain, behave much more nearly like ideal solutes in water. The substances cited by Zwicky all belong to this latter class.

It remains to be seen how far these suggested approximate rules will hold good when a wider range of substances has been investigated.

The apparent molal volumes of amino acids in water are known to be lower than those of most organic compounds, due to electrostriction of the solvent.⁵ The calculations of Zwicky¹ on the heat capacities of electrolyte solutions suggest that the values of apparent molal heat capacity for the amino acids should be lowered by the charged NH_3^+ and COO^- groups which they con-

(5) Cohn, McMeekin, Edsall and Blanchard, *THIS JOURNAL*, **55**, 784 (1934).

TABLE I

APPARENT MOLAL HEAT CAPACITIES IN WATER						
Substance	Temp., °C.	N ₂	φ	Δ	C _p	φ - C _p
Formic acid	16-50	0.02	17		24.6	- 8
Acetic acid	25	.02	38	21	32.2	6
Propionic acid	22-50	.02	63	25	38.8	24
<i>n</i> -Butyric acid	23-50	.02	85	22	44.5	40
Methyl alcohol	20	.03	36		20.4	16
Ethyl alcohol	20	.03	57	21	26.6	30
Propyl alcohol	20	.015	88	31	34.2	54
<i>i</i> -Butyl alcohol	25-29	.02	[160]		42.4	?
Glycine	25	.01	8.0		24 ^a	-16
<i>dl</i> -Alanine	25	.01	38	30	29 ^a	9
<i>dl</i> -Valine	25	.01	85	24		
Glycerol	15	.02	59		51.1	8
Urea	16-20	.01	23		19.3 ^a	4
Dextrose	20	.005	60		54 ^a	6
Sucrose	20	.003	115		102.2 ^a	13

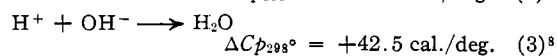
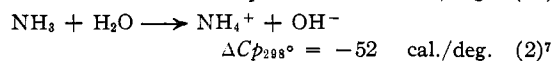
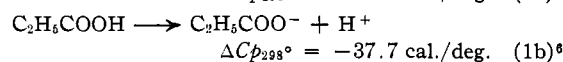
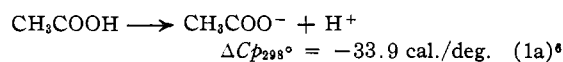
^a Indicates that substance in pure state is a crystalline solid.

N₂ represents approximately the molecular fraction of solute at which the measurement was made; φ represents the apparent molal heat capacity of the solute in calories per degree; Δ represents the increment in φ per CH₂ group in the homologous series studied; C_p is the molal heat capacity of the substances in the pure state at approximately the same temperature at which the solution was measured; φ - C_p represents the deviation between apparent molal heat capacity and heat capacity in the pure state. The value of φ for isobutyl alcohol is abnormally high and is to be regarded as very dubious.

It should be noted that valine differs from alanine by two CH₂ groups, and the given value of Δ is estimated accordingly.

Data on amino acid solutions from Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935). C_p for glycine from Parks, Huffman and Barmore, *THIS JOURNAL*, **55**, 2733 (1933); for alanine from Huffman and Borsook, *ibid.*, **54**, 4297 (1932). Other data from "International Critical Tables," Vol. V, and from Landolt-Börnstein.

tain. The effects due to these groups may be approximately estimated from available data on the ionization of fatty acids, ammonia and water. Reported values of ΔC_p for the ionization of these substances are as follows

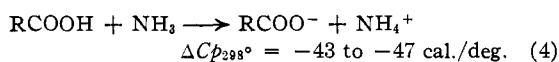


(6) Harned and Ehlers, *THIS JOURNAL*, **55**, 652, 2379 (1933).

(7) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 314. It would be preferable to use data for a primary amine rather than for ammonia in this calculation, but no such data have been reported, so far as I am aware.

(8) Harned and Hamer, *THIS JOURNAL*, **55**, 2194 (1933). See also Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

On adding (1a) or (1b) to (2) and (3) we obtain



This should give the order of magnitude of the molal change in heat capacity accompanying the formation of a carboxyl and an ammonium ion, separated by a large distance, in dilute aqueous solution, whether the charges reside on the same or on different molecules. In α-amino acids, owing to the close proximity of the charges, the effect should be less.

Existing data are insufficient to test the validity of this reasoning, but it may be noted that the value of φ for glycine (Table I) is only 8 calories per mole at 0.5 molal. This is the lowest of all the φ values recorded in Table I, even though glycine is a larger and more complicated molecule than several others given in the table. This would suggest that the hypothesis just stated is at least qualitatively correct. Considerable light might be thrown on the problem by heat capacity measurements on solutions of isomeric amino acids with varying separation of the charged groups (for instance α- and β-alanine, or α- and ε-aminocaproic acid). Measurements on the solution of a betaine and of the uncharged isomeric ester (for instance N-trimethylglycine and N-dimethylglycine methyl ester) should also prove valuable in the study of the influence of electric charge on apparent molal heat capacity.

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The Density of Aqueous Solutions of Lanthanum, Cerous, Praseodymium and Neodymium Chlorides at 25°

BY CHARLES M. MASON AND HOLLIS L. LELAND

A survey of the literature did not reveal any reports on the density of aqueous solutions of the rare earth chlorides. In this Laboratory these data were required for work now in progress. The densities were therefore determined by the pycnometric method with an estimated accuracy of ±0.0002 g. per cc. Inspection of the data showed the density to be a linear function of the percentage composition by weight and on this basis the following empirical formulas were obtained by the method of least squares:

TABLE I

Salt	Density at 25°
LaCl ₃	0.99707 + 0.00912 <i>P</i>
CeCl ₃	.99707 + .00915 <i>P</i>
PrCl ₃	.99707 + .00917 <i>P</i>
NdCl ₃	.99707 + .00920 <i>P</i>

where *P* is the weight percentage of the salt.

These formulas reproduce the experimental data within the above stated accuracy except for the most concentrated solution of lanthanum chloride (4.67%) whose observed density was 1.0403 instead of the 1.0396 calculated.

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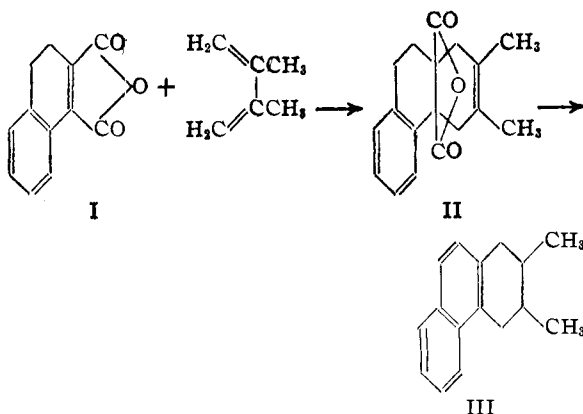
RECEIVED JUNE 11, 1935

COMMUNICATIONS TO THE EDITOR

A NEW PHENANTHRENE SYNTHESIS

Sir:

A new route to polynuclear aromatic and hydroaromatic types containing the phenanthrene ring system has been found in the addition of dienes to cyclic maleic anhydride derivatives such as 3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride (I) [von Auwers and Möller, *J. prakt. Chem.*, 217, 124 (1925)]. The adduct II, m. p. 75.5–76.5° (calcd.: C, 76.57; H, 6.45. Found: C, 76.56; H, 6.44) was obtained from I and 2,3-dimethylbutadiene in 97% yield.



(All melting points reported are corrected.) Hydrogenation, using Adams' catalyst, gave the dihydro adduct, m. p. 117–118°. On fusing II with potassium hydroxide at 320–400° and distilling the product, there was obtained in 70% yield a hydrocarbon (b. p. 194–197° (19 mm.)) having the analysis and properties (resistant to catalytic hydrogenation) corresponding to the formula III. Hydrogen was evolved during the fusion. Dehydrogenation of III with selenium

gave in excellent over-all yield a hydrocarbon which we believe to be pure 2,3-dimethylphenanthrene, m. p. 78–78.5° (calcd.: C, 93.16; H, 6.85. Found: C, 92.86; H, 7.08); picrate, m. p. 146–147°; quinone, m. p. 237.5–238.5° (calcd.: C, 81.32; H, 5.13. Found: C, 81.23; H, 5.37); quinoxaline, m. p. 208–209°. The constants found for the last two derivatives agree well with the values reported by Haworth, Mavin and Sheldrick [*J. Chem. Soc.*, 454 (1934)], but our hydrocarbon melts considerably higher than that synthesized by these investigators. The structure of our material was established by oxidation with nitric acid to pyromellitic anhydride.

In a similar reaction series, using butadiene, we obtained phenanthrene, m. p. 96.5–97.5°, showing no depression when mixed with a purified sample from coal tar (m. p. 97–98°).

Starting with ethyl γ -[1-naphthyl]-butyrate and oxalic ester, we have synthesized 3,4-dihydrophenanthrene-1,2-dicarboxylic acid anhydride, m. p. 263.5–264.5° (calcd.: C, 76.77; H, 4.04. Found: C, 76.83; H, 4.37), and from it the 2,3-dimethylbutadiene adduct, m. p. 196–196.5°. Dehydrogenation of the dihydrophenanthrene derivative with sulfur gave in good yield phenanthrene-1,2-dicarboxylic acid anhydride, m. p. 311–312° (calcd.: C, 77.39; H, 3.25. Found: C, 77.55; H, 3.62). By the same method naphthalene dicarboxylic acid anhydride was obtained from I in 76% yield.

In view of the active interest in the types of compounds made available by these new synthetic methods, and considering the recently reported attempts to apply to the problem other modifications of the Diels–Alder reaction [Cohen,