NOTES

The Preparation of 1,5-Dimethylnaphthalene

By Eleanore W. J. Butz

1,5-Dimethylnaphthalene has been prepared by several procedures.[1] A convenient synthesis, by well-known reactions, which can yield only the 1,5-isomer is presented here. No separation of isomeric products is involved at any stage. 5-Methyl-1-tetralone[2] was prepared by the following steps: *o*-bromotoluene → β-*o*-tolylethyl alcohol → β-*o*-tolylethyl bromide → diethyl β-*o*-tolylethylmalonate → β-*o*-tolylethylmalonic acid → γ-*o*-tolylbutyric acid → 5-methyl-1-tetralone.

Reaction of this ketone with methylmagnesium iodide gave a carbinol which was not purified, but was dehydrated directly by heating in a Claisen flask with a crystal of iodine in a slow stream of carbon dioxide at 200° for one hour. The mixture was then distilled at 28 mm. The main product, presumably 3,4-dihydro-1,5-dimethylnaphthalene (b. p. 130–3° at 25 mm.), was accompanied by 10% of 1,5-dimethylnaphthalene (m. p. 76°). Five grams of the liquid distillate was heated with palladium–charcoal at 250° for two hours. Extraction of this mixture with ether yielded 4 g. of 1,5-dimethylnaphthalene (m. p. 76–7°). After recrystallization from ether and methanol, the product was dried at 35° and 80 mm. for one hour; m. p. 80°; picrate, m. p. 137°.

Anal.[3] Calcd. for $C_{12}H_{12}$: C, 92.31; H, 7.69. Found: C, 92.19; H, 7.73.

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(1) Vesely and Stursa, *Coll. Czechoslov. Chem. Commun.*, **3**, 430 (1931); Anderson and Short, *J. Chem. Soc.*, 485 (1933); Manske and Ledingham, *Can. J. Research*, **17B**, 14 (1939).

(2) Harvey, Heilbron and Wilkinson, *J. Chem. Soc.*, 423 (1930).

(3) Microanalysis by Arlington Laboratories.

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The Heat of Solution of Gadolinium Sulfate Octahydrate and the Entropy of Gadolinium Ion

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As an aid to a better understanding of the process of hydration of ions from the thermodynamic viewpoint, additional ionic entropy values for monatomic tripositive ions are of considerable value. As a step in this direction an entropy value for Gd^{+++} has been calculated in the usual manner from entropy, heat of solution and estimated free energy of solution data.

The heat capacity of $Gd_2(SO_4)_3\cdot 8H_2O$ has been measured by Giauque and Clark[1] and Ahlberg and Clark.[2] On the basis of these measurements Kelley[3] has obtained 155.7 cal./deg. for the entropy which includes the magnetic entropy $R \ln 8$ for each gram ion of Gd^{+++}.

The heat of solution of $Gd_2(SO_4)_3\cdot 8H_2O$ was measured in a calorimeter already described in This Journal.[4] The sample used in these measurements was prepared from some gadolinium oxalate of about 95% purity which was donated by Dr. Herbert McCoy. The impurity is probably neighboring rare earths which would lead to no appreciable error in the measurements. The oxalate was ignited to the oxide, dissolved in sulfuric acid and recrystallized. After attaining constant water content at room temperature, the hydrated sulfate was, of necessity, powdered to assure a rapid rate of solution. An analysis for volatile constituents of the salt by ignition to the oxide indicated a deficiency of 0.3% as compared with the calculated value. A portion of this may be attributed to the impurities in the sample used. The results of the experiments are tabulated in Table I. The final volume in each case was 1050 cc. As no heat of dilution data are available for this salt, the measured value will be used uncorrected in the following calculations. The error involved from this procedure will be taken into account in the estimated error quoted for the ionic entropy.

Table I

Heat of Solution of $Gd_2(SO_4)_3\cdot 8H_2O$ at 25°

Sample, wt. g.	Mole	Observed heat absorbed, cal.	Molal heat absorbed, cal.
13.3563	0.01788	−118.66	−6640
13.0707	.01750	−118.56	−6775
			−6710 ± 100

Interpolation of the "I. C. T."[5] values for the solubility of $Gd_2(SO_4)_3\cdot 8H_2O$ gives 0.041 M for the saturated solution at 25°. Since no activity coefficient data are available for $Gd_2(SO_4)_3$, the activity coefficient was estimated from data for $La_2(SO_4)_3$ and $In_2(SO_4)_3$. For 0.01 M $La_2(SO_4)_3$,

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(1) Giauque and Clark, This Journal, **54**, 3135 (1932).

(2) Ahlberg and Clark, *ibid.*, **57**, 437 (1935).

(3) Kelley, "Bureau Mines Bulletin 394."

(4) Pitzer, This Journal, **59**, 2365 (1937).

(5) "International Critical Tables," Vol. IV, p. 227.

Rodebush[6] calculated γ to be 0.15 from freezing point lowering data.[7] An extrapolation with the aid of cryoscopic data obtained by Noyes and Johnston[8] for the same salt resulted in the approximate value 0.05 for γ at saturation at 25°.

In a study of $In_2(SO_4)_3$ solutions Hattox and DeVries[9] determined the activity coefficient of this salt from e. m. f. measurements. By interpolation γ has the value 0.06 for $In_2(SO_4)_3$ at 0.04 *M*. Taking an average of 0.055 at 0.041 *M* for γ for $Gd_2(SO_4)_3$ the free energy of solution to form the hypothetical 1 *M* solution is

$$\begin{aligned}\Delta F &= -RT \ln (\gamma m)^5(2^2 \cdot 3^3)\\ &= -1363.8 \log (0.055 \times 0.041)^5(2^2 \cdot 3^3)\\ &= 15{,}200 \pm 1000 \text{ cal.}\end{aligned}$$

Knowing the heat of solution and an approximate free energy of solution for this salt, the entropy of solution at 25° was calculated to be −73.5 cal./deg. mole. The calculation of the relative partial molal entropy of Gd^{+++}, involving the entropy of $Gd_2(SO_4)_3 \cdot 8H_2O$,[3] the partial molal entropy of $SO_4^{=}$[10] (4.4 cal./deg. mole) and the entropy of water[11] (16.75 cal./deg.) may now be completed as follows

$$\begin{aligned}\bar{S}^\circ_{Gd^{+++}} &= {}^1/_2(\Delta S_{soln.} + S^\circ_{Gd_2(SO_4)_3 \cdot 8H_2O} - 3\bar{S}^\circ_{SO_4^{=}} - 8S^\circ_{H_2O})\\ &{}^1/_2(-73.5 + 155.7 - 13.2 - 134.0) = -32.5 \pm 4 \text{ cal./deg. mole}\end{aligned}$$

The assignment of an entropy value to Gd^{+++} supplements data for two other tripositive ions, Fe^{+++} and Al^{+++}, and now makes possible a comparison of hydration entropies of tripositive ions with mono- and dipositive types. Heretofore, hydration entropies, the calculation of which has already been described,[12] have been found best related to the reciprocal of the ion radius in a linear manner for singly and doubly charged ions.[12,13] If such calculations are made for Gd^{+++}, Fe^{+++} and Al^{+++} a similar relationship exists.

As an empirical rule the entropy of hydration of singly, doubly and triply charged ions may now be approximately represented as follows

$$\Delta S_{hyd.} = -An/r + B_n$$

where *A* is a constant, common to all ions, having the value 80, *n* is the number of charges on the ion and B_n has the values 28, 40 and 67 for singly, doubly, and triply charged ions, respectively. What the significance of the above expression may be is not known. However, it does indicate that hydration entropies may be more closely related to the first power of the charge than to the square as previously supposed.[13]

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[6] Rodebush, THIS JOURNAL, **48**, 709 (1926).

[7] Hovorka and Rodebush, *ibid.*, **47**, 1614 (1925).

[8] Noyes and Johnston, *ibid.*, **31**, 987 (1909).

[9] Hattox and DeVries, *ibid.*, **58**, 2126 (1936).

[10] Latimer, Pitzer and Smith, *ibid.*, **60**, 1829 (1938).

[11] Giauque and Stout, *ibid.*, **58**, 1144 (1936).

[12] Latimer, Pitzer and Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

[13] Latimer, *Chem. Rev.*, **18**, 349 (1936).

Bieugenol in a Commercial Geraniol[1]

BY HOWARD A. JONES AND H. L. HALLER

During an examination of commercial geraniol prepared from Java citronella oil for use in Japanese beetle baits, a gelatinous precipitate was formed when a sample of the geraniol was heated. On cooling the geraniol, the product did not redissolve. It was separated by filtration, and the adhering geraniol was removed with alcohol and ether. Chemical examination proved it to be the zinc salt of bieugenol (3,3′-diallyl-5,5′-dimethoxy-6,6′-dihydroxybiphenyl). Eugenol, a known constituent of Java citronella oil, was also shown to be present in the commercial geraniol.

When the geraniol was washed with water, the zinc was removed as a water-soluble salt, but the aqueous solution contained no free or combined phenols. When the water-washed oil was heated, no precipitate was formed. Free bieugenol was isolated from the residue remaining after steam distillation of a sample of the geraniol. Thus it is shown that bieugenol is present as such in the commercial geraniol and that the formation of the insoluble zinc salt is promoted by heat.

The zinc in the geraniol undoubtedly came from the galvanized drums in which geraniol is frequently stored, and the bieugenol probably resulted from the oxidation of eugenol. Commercial geraniol used for Japanese beetle baits contains, in addition to the free eugenol, alcohols, esters, terpenes and sesquiterpenes. Whether or not these compounds or the zinc salt has any role in promoting the formation of bieugenol is not known. Additional information on this point would be of interest as possibly leading to a new method for the preparation of bieugenol as well as other biphenols. Such a study is beyond the scope of our work.

Experimental

Zinc Bieugenol.—A commercial geraniol (1332 g.) was subjected to fractional distillation at a pressure of 2 to 4

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[1] Not subject to copyright.