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

$$\begin{aligned}\Delta F &= -RT \ln (\gamma m)^5(2^2\cdot3^3)\\ &= -1363.8 \log (0.055 \times 0.041)^5(2^2\cdot3^3)\\ &= 15{,}200 \pm 1000 \text{ cal.}\end{aligned}$$

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 $Gd_2(SO_4)_3\cdot8H_2O$,[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

$$\bar{S}^\circ_{Gd^{+++}} = {}^1/_2(\Delta S_{soln.} + S^\circ_{Gd_2(SO_4)_3\cdot8H_2O} - 3\bar{S}^\circ_{SO_4^{=}} - 8S^\circ_{H_2O}$$
$${}^1/_2(-73.5 + 155.7 - 13.2 - 134.0) = -32.5 \pm 4 \text{ cal./deg. mole}$$

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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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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[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).

[1] Not subject to copyright.

mm. and a temperature in the still of 100 to 150°. The gelatinous precipitate that separated was removed by filtration at an early stage in the distillation. After being washed with ethanol and ether and dried to constant weight in a vacuum desiccator, it weighed 1.17 g., or about 0.09% of the original weight. On ignition the precipitate gave 19.7% ash (calcd. for $C_{20}H_{20}O_4Zn$, 20.8% ZnO). The ash gave qualitative tests for zinc. Another portion of the dried precipitate, after being suspended in water, acidified with dilute sulfuric acid, and extracted with ether, gave after removal of the solvent a white crystalline solid. After several recrystallizations from dilute ethanol it melted at 106°.[2] In ethanol solution the compound gave a deep blue color with ferric chloride. When it was mixed with a sample of pure bieugenol prepared from eugenol by the method of Erdtman,[3] there was no depression of the melting point. On catalytic hydrogenation in ethanol with Adams platinum oxide as catalyst, it was readily reduced with the formation of tetrahydrobieugenol, which after recrystallization from ethanol melted at 151°. Erdtman gives 152° as the melting point of this compound.

Eugenol.—A portion (178 g.) of that fraction of the crude geraniol remaining after three-fourths by volume had been distilled was diluted with ether and extracted with 5% aqueous sodium carbonate and then with 5% aqueous sodium hydroxide. The latter extract was acidified and extracted with ether. The water-washed ether extract was dried over sodium sulfate. After removal of the ether, there remained 4.5 g. of oil having a clove-like odor. It was purified by distillation under reduced pressure. It distilled at 142–142.5° (23.5 mm.). The distillate ($n^{30}\text{D}$ 1.5345) gave a deep blue color with ferric chloride. The 3,5-dinitrobenzoate prepared by the method of Phillips and Keenan[4] had a melting point of 130.5°. A mixture with the 3,5-dinitrobenzoate of eugenol gave no depression of the melting point.

The original sample of crude geraniol gave 1.8% total material soluble in 5% sodium hydroxide.

Zinc in Water Washings.—Crude geraniol (445 g.) was diluted with ether and extracted with water. When the water solution had been evaporated practically to dryness, 0.5 g., or about 0.1%, of material was obtained. On ignition an ash was obtained which gave qualitative tests for zinc. A portion of the water-soluble solid was acidified and extracted with ether. The evaporated extract gave no color with ferric chloride.

A portion of the water-insoluble crude geraniol from the water washing gave no precipitate when boiled for about fifteen minutes. A similar portion of the original unwashed crude geraniol gave a voluminous, gelatinous precipitate after boiling for about two minutes.

Bieugenol in Residue from Steam Distillation.—A portion of the crude geraniol (888 g.) was subjected to steam distillation until about 95% by weight had distilled. The residue was extracted with ether, and the ether solution was extracted successively with 5% aqueous solutions of potassium bicarbonate, sodium carbonate and sodium hydroxide. The final extract yielded, after acidification, extraction with ether and removal of the solvent, a product consisting of crystalline material and a brown, viscous oil. The yield was 0.84 g. (about 0.1% of the sample). The mixture was washed with dilute ethanol, and the crystalline residue was recrystallized several times from the same solvent. The product melted at 106° and showed no depression of melting point in admixture with bieugenol prepared by the method of Erdtman.[3]

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[2] All melting points are corrected.

[3] Erdtman, *Biochem. Z.*, **258**, 172 (1933).

[4] Phillips and Keenan, THIS JOURNAL, **53**, 1924 (1931).

Factors Influencing Polysulfone Formation

BY M. S. KHARASCH AND E. STERNFELD

In the course of an investigation involving sulfur dioxide and olefins we were concerned with the possibility of polysulfone formation as an undesirable side reaction. We found that mineral acids, in the presence of a peroxide such as ascaridole, markedly catalyzed this reaction for several olefins which did not readily form polysulfones. Recently, Marvel and Glavis[1] have found peracetic acid a more potent catalyst than acyl peroxides in the formation of polysulfones from vinyl and allyl chlorides. From our experiments, it would seem that a mixture of ascaridole and hydrochloric, hydrobromic, or sulfuric acid is at least as effective as peracetic acid in polysulfone formation from trimethylethylene and allyl or vinyl chlorides.

Allyl bromide does not give a polysulfone under any conditions. What is more remarkable, we found it to be a powerful inhibitor for the formation of polysulfones from other olefins. Thus, allyl chloride mixed with five mole per cent. of allyl bromide does not react to any extent with sulfur dioxide even in presence of ascaridole and mineral acid, whereas without the allyl bromide the yield of allyl chloride polysulfone is practically quantitative. A large excess of ascaridole over the allyl bromide (10 moles to 1) brought about the formation of allyl chloride polysulfone. The yield, however, was poor (less than 20%). Allyl bromide was also a powerful inhibitor for polysulfone formation from cyclohexene and pentene-2 when (following the procedure of Frederick, Cogan and Marvel[2]) aqueous hydrogen peroxide was used as a catalyst. In these cases, the addition of mineral acids overcame this inhibition.

It is difficult to explain the action of allyl bromide as an inhibitor. Attempts to substitute for

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[1] Marvel and Glavis, *ibid.*, **60**, 2622 (1938).

[2] Frederick, Cogan and Marvel, *ibid.*, **56**, 1815 (1934).