The data[9] obtained on cellulose, silk and wool–water systems are plotted for comparison in Figs. 2, 3 and 4, according to equation (1) and equation (2), respectively. It is noted that for $P/P_0 < 0.5$, the data follow the straight line relationship called for by equation (2). Thereafter a more rapid increase is observed. The agreement over such a wide range is remarkable although unexpected on the basis of the assumptions underlying the derivation of equation (2). On the other hand it will be seen that the parameter μ starts out with a negative value, increases slowly and then assumes a fairly constant positive value of about 1.0–1.25 for $P/P_0 > 0.6$. In terms of the volume fraction v_1 of water the total range of measurements corresponds to $0.01 < v_1 < 0.26$. In the region of $0.10 < v_1 < 0.26$, equation (1) is obeyed by cellulose and silk. In wool μ varies approximately from 0.93 to 1.05 over the range $0.18 < v_1 < 0.26$. The various energy and entropy contributions to the quantity μ are different at high and low polymer concentrations.[10] These changes can lead to a variation of the "constant" μ. For rubber–benzene mixtures, the only system so far studied over the whole concentration range,[11,12] no significant change of μ was observed. In any case the deviations from equation (1) obtained by us over a relatively narrow range of volume fractions are too large to be caused by the above-mentioned effect. The limiting values obtainable from these data are $\mu = 1.25$, 1.15, and 1.05 for cellulose, silk and wool, respectively. If the polymer is regarded effectively as a network, allowance must be made for the free energy change accompanying elastic distortion during sorption. The model of a Hookean isotropic medium, subject to a deformation dependent on the concentration, leads merely to a slight reduction in the μ-values reported. These are larger than those usually found by means of solution or swelling measurements for other polymers.[13,14] Also, an examination of the temperature coefficients of μ leads to negative values of the heat term and reduced entropies which indicate that mixing is not a random process. In view of the nature of the systems considered here this is not surprising.

These results provide some support for the concept mentioned earlier. They suggest that the combination of water with these textile materials in the limit of low vapor pressures can be described in terms of adsorption theory. However, as one approaches the limit of high vapor pressures the system can be analyzed in terms of a theory of polymer–liquid mixtures. In the intermediate region between the two extremes a gradual transition occurs. It will be of interest to study the effect of variation in the nature of the liquid upon the properties of these systems.

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[10] P. J. Flory, *J. Chem. Phys.*, **13**, 453 (1945).

[11] G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).

[12] G. Gee and W. J. C. Orr, *ibid.*, **42**, 507 (1946).

[13] M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).

[14] R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **2**, 157 (1947).

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p-Aminosalicylic Acid (4-Amino-2-hydroxybenzoic Acid)

By John T. Sheehan

When *m*-aminophenol and ammonium carbonate react under pressure an acid is obtained which melts at 148°.[1] In the original publication no identification is made beyond that of *m*-aminophenolcarboxylic acid. To determine whether the acid formed is *p*-aminosalicylic acid (4-amino-2-hydroxybenzoic acid) which is of current interest in the chemotherapy of tuberculosis,[2,3] the preparation was repeated in this Laboratory.

It was found that the acid could be isolated directly from the reaction mixture rather than as the hydrochloride as originally described. It could also be precipitated as the barium salt, from which the acid can be readily obtained in purer form. The identity of the acid was established as *p*-aminosalicylic acid by converting it through the diazonium salt into 4-chlorosalicylic acid and comparing this with a sample of the same compound prepared by reacting 2,4-dichlorobenzoic acid with barium hydroxide. Finally a comparison of antibacterial activity[4] disclosed no difference between the acid prepared by the present method and another sample of *p*-aminosalicylic acid.[5]

Experimental

***p*-Aminosalicylic Acid.**—A mixture of 150 g. (1.37 moles) of *m*-aminophenol, 600 g. of ammonium carbonate (6.25 moles) and 750 ml. of water was heated in a rocker-type autoclave at 110° for twelve hours. The mixture was filtered and the filtrate concentrated *in vacuo* to a volume of 450 ml. The solution was then acidified to *p*H 5 and extracted with three 250-ml. portions of ether, from which 75 g. of *m*-aminophenol was recovered. The aqueous solution from the extraction was adjusted to *p*H 2–3 and the *p*-aminosalicylic acid filtered off and washed with water. The product weighed 47 g. and was crystallized from warm alcohol. Alternatively, it can be purified through the barium salt. A 22% yield of product melting at 146–147°[6] was obtained. *Anal.* Calcd. for $C_7H_7NO_3$: C, 54.90; H, 4.57; N, 9.15. Found: C, 55.03; H, 4.91; N, 9.13.

4-Chlorosalicylic Acid.—Fifteen and three-tenths grams (0.1 mole) of the above acid were diazotized and con-

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[1] German Patent 50,835; *Friedlander*, **2**, 139 (1887–90).

[2] Lehman, *Lancet*, **250**, 15 (1946).

[3] Youmans, *Quart. Bull. Northwestern Univ. Med. School*, **20**, 420 (1946); *C. A.*, **41**, 1011 (1947).

[4] The chemotherapeutic investigation was made under the direction of Dr. G. W. Rake in the Division of Microbiology of this Institute.

[5] Supplied by Calco Chemical Division, American Cyanamid Co., Bound Brook, New Jersey.

[6] The reported melting point of *p*-aminosalicylic acid is 220° (dec.); Seidel, *Ber.*, **34**, 4351 (1901); Seidel and Bittner, *Monatsh.*, **23**, 415 (1902). Since the acid was prepared by reducing *p*-nitrosalicylic acid with tin and hydrochloric acid it seems likely that the melting point of the hydrochloride, which we found decomposes about this temperature, is recorded despite the fact that the empirical formula and analyses given are for the free acid.

verted to the chloride.[7] Nine grams of 4-chlorosalicylic acid was obtained, m. p. 211° after crystallization from water. No depression in m. p. was observed when this product was mixed with the substance prepared below. *Anal.* Calcd. for $C_7H_5O_3Cl$: C, 48.71; H, 2.92; Cl, 20.54. Found: C, 48.52; H, 3.04; Cl, 20.69.

A mixture of 6 g. of 2,4-dichlorobenzoic acid, 20 g. of barium hydroxide hydrate, 60 ml. of water and 0.5 g. of copper-bronze was heated in a sealed tube for six hours at 160-170°. The product was filtered and then suspended in water and decomposed with hydrochloric acid. Crystallized from hot water, the chlorosalicylic acid, 2.9 g, melted at 211-212°. 4-Chlorosalicyclic acid is reported to melt at 211°; 2-chloro-4-hydroxybenzoic acid at 159°.[8]

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[7] The procedure described in "Org. Syn.," Coll. Vol. I, p. 163, 1st ed., was followed except that threefold volumes of acid were employed to facilitate the reaction of the insoluble acid hydrochloride and its insoluble diazonium salt. In addition, chlorobenzene was added during the decomposition of the diazonium salt, to extract the product as formed.

[8] Hodgson and Jenkinson, *J. Chem. Soc.*, 1740 (1927).

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The Preparation of Phthalaldehyde

BY S. WAWZONEK AND R. E. KARLL[1]

Varying yields have been reported for the preparation of phthalaldehyde from *o*-xylene.[2] It has been found that, by using all-glass apparatus and the procedure described below, *o*-xylene and *o*-methylbenzyl bromide can be brominated in 64% yield to $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene. Under similar conditions *o*-methylbenzyl chloride gives the same yield of a mixture of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene and $\alpha,\alpha,\alpha',\alpha'$-chlorotribromo-*o*-xylene. *o*-Methylbenzyl chloride is the most suitable starting material since the best commercially available *o*-xylene is only 90% pure while *o*-methylbenzyl bromide is a powerful lachrymator.

The tetrahalo-*o*-xylenes can be hydrolyzed to phthalaldehyde of melting point 55.5° in a 90% yield by the method of Thiele.[2a] The only modification made in this procedure was to saturate the aqueous solution of the aldehyde with sodium chloride instead of sodium sulfate.

Experimental[3]

$\alpha,\alpha,\alpha',\alpha'$-Tetrahalo-*o*-xylene.—*o*-Methylbenzyl chloride[4] was brominated according to the directions given in "Organic Syntheses"[5] with the following modifications. All-glass equipment was used together with a Trubore glass stirrer. From 132.6 g. of *o*-methylbenzyl chloride, 245 g. of product was obtained by taking up the reaction mixture in hot chloroform (300 ml.) and cooling; m. p., 106°. Repeated recrystallizations from ethanol gave a white crystalline compound melting at 110-111°. A mixture with tetrabromo-*o*-xylene (m. p., 115.5°) melted at 112°.

Anal. Calcd. for $C_8H_6ClBr_3$: Br, 63.6. Calcd. for $C_8H_6Br_4$: Br, 78.20. Found: Br, 72.89, 72.97.

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[1] Abstracted from a thesis by R. E. Karll presented to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the M.S. degree. June, 1947.

[2] (a) Thiele and Gunther, *Ann.*, **347**, 106 (1906); Thiele and Weitz, *ibid.*, **377**, 8 (1910); (b) Sandstrom and Lillevik, *Ind. Eng. Chem., Anal. Ed.*, **13**, 781 (1941); (c) Fieser and Pechet, THIS JOURNAL, **68**, 2577 (1946).

[3] Melting points are corrected.

[4] Smith and Spillane, THIS JOURNAL, **62**, **2640** (1940).

[5] "Organic Syntheses," Vol. 20, John Wiley and Sons, Inc., New York, N. Y., p. 92.

DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA RECEIVED NOVEMBER 13, 1947

Ethyl Acetamidoacetoacetate

BY RICHARD H. WILEY AND OLIN H. BORUM

The reduction of oximinoacetoacetic ester over palladium catalyst in acetic anhydride gives a product, m. p. 46-47.5°, which has been characterized as acetamidoacetoacetic ester, $CH_3CONHCH(COCH_3)CO_2C_2H_5$. The only known previous reference[1] to this compound describes a less convenient method of preparation and reports a melting point of 141°.

Experimental

Ethyl Oximinoacetoacetate.—This compound was prepared by the method of Adkins and Reeve.[2]

Ethyl Acetamidoacetoacetate.—Thirty-two grams of ethyl oximinoacetoacetate and 6.9 g. of palladium catalyst[3] were shaken in 50 ml. of acetic anhydride at room temperature under 30 lb. hydrogen pressure for ten hours. After separating from the catalyst and removing the excess acetic anhydride, 35 g. of acetamidoacetoacetic ester b. p. 128-140° (3-4 mm.) was obtained. Refractionation gave 25.7 g. b. p. 125-132° (3-4 mm.) which solidified on standing, m. p. 46-47.5°.

Anal. Calcd. for $C_8H_{13}O_4N$: C, 51.33; H, 7.0; N, 7.48. Found: C, 51.13; H, 7.0; N, 7.50.

This solid gave qualitative tests for carbonyl with 2,4-dinitrophenylhydrazine reagent and for enol with alcoholic ferric chloride. Reaction with phenylhydrazine in ether, according to the procedure of Michael[4] for the preparation of the phenylhydrazone of acetoacetic ester, gave a yellow precipitate of the phenylhydrazone, m. p. 131.5-132.5°.

Anal. Calcd. for $C_{14}H_{19}O_3N_3$: C, 60.63; H, 6.9; N. 15.15. Found: C, 60.43; H, 6.96; N, 15.10.

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[1] Cerchez and Colesiu, *Compt. rend.*, **194**, 1954 (1932).

[2] Adkins and Reeve, THIS JOURNAL, **60**, 1328 (1938).

[3] R. Mozingo, *et al.*, *ibid.*, **67**, 2093 (1945). Washed free of chloride.

[4] A. Michael, *Am. Chem. J.*, **14**, 519 (1892).

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The Decomposition of *o*-Methoxybenzene Diazonium Chloride

BY H. E. WOODWARD AND A. A. EBERT, JR.

M. L. Crossley and others[1] have reported that the decomposition of *o*-methoxybenzene diazonium chloride can be assumed to consist of two de-

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[1] THIS JOURNAL, **69**, 1160 (1947).