modynamic" dissociation constants[21] were calculated from $pK_{1\text{therm.}} = pK_{1\text{incomp.}} + 0.505\ \mu^{0.5}$ (i) and $pK_{2\text{therm.}} = pK_{2\text{incomp.}} + 1.515\ \mu^{0.5}$ (ii), where $pK_{1\text{therm.}} = -\log K_{1\text{therm.}}$ etc., and the total ionic strength, which was deduced from the expression[8]

$$\mu = 0.5\left(a + h + c\left\{\frac{1}{(h/K_1 + 1 + K_2/h)} + \frac{4}{(h/K_2 + 1 + h^2/K_1K_2)}\right\}\right)$$

where c is total acid concentration, a is concentration of sodium hydroxide added, h is hydrion concentration, and K_1 and K_2 are the "incomplete" (previously termed "classical") values.

The use of the approximate expressions (i) and (ii) over the concentration range ($\mu = 0.0015$ to 0.006) that we have employed is justified by the following considerations. Morton[22] has deduced the equation

$$p_k = p\text{H} + \log\,[\text{Acid}]/[\text{Salt}] + \log f_a/f_s$$

in which f_a and f_s are the activity coefficients of the undissociated acid and of the salt anions or of the acid anions of lower and higher valency, respectively. This may be written in the form

$$\begin{aligned} pK_{\text{therm.}} &= pK_{\text{incomp.}} + \log f_a/f_s \\ &= pK_{\text{incomp.}} + (n - 0.5)\mu^{0.5} - B\mu \end{aligned}$$

since $\log f_a/f_s = (n - 0.5)\mu^{0.5} - B\mu$; n is the basicity of the acid. For phthalic acid, which is the acid most closely allied to those that we have studied, the highest value of B found by Morton was approximately 1 and this was in the presence of $M/3$ potassium sulfate. It can be readily shown that with $B = 1$ in the most concentrated solutions that we have employed, the maximum error introduced by the neglect of this term is *ca.* 1%. Actually the error will be much less than this.

Summary

The thermodynamic dissociation constants of malonic, succinic and glutaric acids have been determined by potentiometric titration with the quinhydrone electrode. The values for the primary dissociation constants agree within 2–4% with those determined by conductivity.

LONDON, S. E. 18, ENGLAND RECEIVED DECEMBER 20, 1935

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[21] It is appreciated that this term should be strictly confined to values obtained by experimental technique which does not involve uncertainties in liquid junction potentials and by strict thermodynamic methods, as in the precise work of Harned and co-workers. It is believed, however, that the approximations introduced are sufficiently precise for the ultimate accuracy of 2–3% which is claimed to justify the use of the term.

[22] Morton, *J. Chem. Soc.*, 1406 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

β-Amoxyethyl Esters of *p*-Aminobenzoic Acid

BY H. V. ASHBURN, A. R. COLLETT AND C. L. LAZZELL

In continuation of our work on the β-alkoxyethyl esters of *p*-aminobenzoic acid,[1] we have prepared a series of six amoxyethanols, three of which are new, together with the corresponding *p*-nitro and *p*-aminobenzoates. The alcohols used were purified by fractional distillation, until a sample having a boiling point range of 0.5° or less was obtained.

β-Amoxyethanols

The β-amoxyethanols were prepared by heating the desired alcohol with ethylene oxide in the presence of a small amount of sulfuric acid as a catalyst[2] except in the case of the tertiary amoxyethanol, for which acid aluminum fluosilicate was used as a catalyst.[3]

The method was as follows: 20 to 30 moles of the alcohol, 7 moles of ethylene oxide, and 1 cc. of concentrated sulfuric acid were placed in an autoclave and heated at 130–150° for eight to ten hours. The autoclave was then emptied and the contents fractionally distilled. The tertiary amyl compound was prepared by using acid aluminum fluosilicate as the catalyst and heating at 130–150° for twenty-five hours.

These compounds are all colorless, sweet smelling liquids, very soluble in alcohol and ether. The iso primary amyl, active primary amyl and tertiary amyl compounds are all appreciably soluble in water at 25° while the *n*-primary amyl, secondary amyl and active secondary amyl compounds are only slightly soluble.

Table I lists the yields and physical constants of all the amoxyethanols prepared, together with the analyses of the new compounds. The tertiary butoxyethanol has been prepared since the only physical property recorded in the literature is the boiling point, 150–153°. Its density is 0.8935

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[1] Ashburn, Collett and Lazzell, THIS JOURNAL, **57**, 1862 (1935).

[2] German Patent 580,075, July 5, 1933; *C. A.*, **27**, 4814 (1933).

[3] French Patent 39,773, Feb. 17, 1931; *C. A.*, **26**, 4826 (1932).

TABLE I

β-AMOXYETHANOLS, ($ROCH_2CH_2OH$)

Amyl group	Yield, %	B. p.,		$d^{25}_{abs.}$	$n^{25}D$	C, %	H, %
		°C.	Mm.			calcd. 63.6	calcd. 12.2
$CH_3(CH_2)_4$-[a]	34	188.3	751.1	0.8893	1.42266	..	...
$(CH_3)_2CH(CH_2)_2$-	32	179.8	750.1	.8884	1.42092	..	...
$(CH_3)(C_2H_5)CHCH_2$-	43	176.8	748.0	.8978	1.42197	63.1	12.00
$(C_2H_5)_2CH$-	38	172.6	746.4	.9151	1.42200	63.3	12.02
$(CH_3)(n\text{-}C_3H_7)CH$-	34	173.8	746.0	.9144	1.42125	63.3	11.70
$(C_2H_5)(CH_3)_2C$-[b]	18	168.4	745.4	.9145	1.42322	63.5	11.90

[a] Recorded in the literature as 181° at 745 mm. [Cretcher and Pittenger, THIS JOURNAL, **46**, 1503 (1924)] and as 85.5–86.5° at 23 mm. [Tallman, THIS JOURNAL, **56**, 126–129 (1934)]. [b] This compound was analyzed since the only property listed in the literature was the boiling point given as 50–55° at 3 mm. [U. S. Patent 1,968,033 (1934); *C. A.*, **28**, 5832 (1934)].

TABLE II

p-NITROBENZOATES ($ROCH_2CH_2OOCC_6H_4NO_2(p)$)

Amyl group	% yield	B. p., °C., 4 mm.	$d^{25}_{abs.}$	$n^{25}D$	γ^{25}	N, % (Calcd. 4.98) Found	
$CH_3(CH_2)_4$-	87	191.5–192.5	1.1301	1.5141	36.1	4.95	4.90
$(CH_3)_2CH(CH_2)_2$-	80	184.1–185.1	1.1287	1.5136	34.9	4.87	4.88
$(CH_3)(C_2H_5)CHCH_2$-	89	188.1–189.0	1.1276	1.5129	35.1	4.85	4.87
$(C_2H_5)_2CH$-	87	183.0–184.0	1.1539	1.5138	36.2	4.93	5.01
$(CH_3)(n\text{-}C_3H_7)CH$-[a]	87	186.6–187.6	1.1633	1.5164	36.0	5.18	4.96
$(C_2H_5)(CH_3)_2C$-	89	164.0–166.0[b]	....	....	..	4.90	4.88

[a] Crystallized after setting for several weeks; recrystallized from ligroin gave a melting point of 74.5°. [b] Pressure 0.42 mm.

($d^{25}_{abs.}$), refractive index is 1.41322 $n^{25}D$, and it boils at 151.3 under 750 mm. pressure.[3]

All boiling points were taken with a certified thermometer completely immersed in the vapor. Refractive indices were taken with a dipping refractometer at 25°. The yields are based upon the amount of ethylene oxide used.

***p*-Nitrobenzoates.**—The *p*-nitrobenzoates of these β-amoxyethanols were prepared according to the method of Conn, Collett and Lazzell.[4] These esters are viscous, practically odorless liquids having a pale yellow color. They are insoluble in water but soluble in all the common organic solvents. Table II lists the analyses, physical constants and yields of all the new *p*-nitrobenzoates prepared.

The analyses were made by titration with titanous chloride. Refractive indices were determined by means of an Abbé refractometer at 25°. Surface tensions were obtained by means of a du Noüy tensiometer at 25° and Harkins' correction for the ring method was applied. The yields are based upon the amount of glycol ether used.

***p*-Aminobenzoates.**—The *p*-aminobenzoates were prepared from the corresponding nitro compounds as described in the previous article,[1] except for the distillation. After the removal of the alcohol, a small amount of zinc dust was introduced into the distilling flask and the distillation carried out at pressures of 1 mm. or less. This removed the red by-product which was formed upon exposure of the reduced solution to the air.

Table III lists the analyses and yields of the *p*-aminobenzoates, and the melting points of the picramides.

TABLE III

p-AMINOBENZOATES ($ROCH_2CH_2OOCC_6H_4NH_2$-*p*)

Amyl group	Yield, %	N analyses, % (Calcd. 5.58) Found		M. p., °C., picramide
$CH_3(CH_2)_4$-[a]	85	5.61	5.70	115.5
$(CH_3)_2CH(CH_2)_2$-	81	5.49	5.55	140.9
$(CH_3)(C_2H_5)CHCH_2$-	83	5.46	5.43	129.1
$(C_2H_5)_2CH$-	80	5.51	5.68	136.0
$(CH_3)(n\text{-}C_3H_7)CH$-	80	5.50	5.52	120.8
$(C_2H_5)(CH_3)_2C$-	76	6.07	5.48	134.9

[a] Fine white needles from ligroin, melting point 56.8°.

The picramides were prepared by the method given by Mulliken.[5] The *p*-aminobenzoates are all viscous oils at room temperature with the exception of the *n*-amyl compound. The yields are based upon the amount of nitro compound used. The picramides are all fine yellow needles, having a sharp melting point.

The physiological properties of the *p*-aminobenzoates are now being investigated.

The authors wish to express their appreciation to the Carbide and Carbon Chemicals Corpora-

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(4) Conn, Collett and Lazzell, THIS JOURNAL, **54**, 4370 (1932).

(5) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1916, Vol. II, p. 32.

tion for the generous supply of ethylene oxide furnished for this investigation.

Summary

Three new β-amoxyethanols, six new β-amoxyethyl esters of *p*-nitrobenzoic acid and six new β-amoxyethyl esters of *p*-aminobenzoic acid have been prepared and some of their physical constants determined.

MORGANTOWN, WEST VIRGINIA RECEIVED JUNE 13, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Succinic-α-d,α'-d Acid and its Derivatives. II. Stereochemistry of the Type RR'CHD

BY MARLIN T. LEFFLER[1] AND ROGER ADAMS

The effect of deuterium upon the optical activity of organic molecules and the possibility of obtaining an answer to the question as to whether RR'CHD may be optically active has engaged the attention of investigators in several laboratories.[2]

Schoenheimer and Rittenberg[3] compared the optical activity of coprostanone-d_2 and coprostanone and noted that the difference in optical activity was very small, if at all appreciable. Erlenmeyer and Gärtner[4] were unable to resolve phenylpropionic-α-d,β-d acid of which they obtained an impure sample by reduction of cinnamic acid with deuterium iodide and phosphorus.

In the research now reported the reduction of diethyl fumarate and diethyl maleate was carried out using practically 100% deuterium in the presence of platinum catalyst. The resulting diethyl succinate-α-d,α'-d corresponds to the stereochemical R'CHD-CHDR' type, separable into a *meso* and a *racemic* modification. It is well known that the action of permanganate on maleic acid produces *meso*-tartaric acid while the *racemic* modification results from fumaric acid. Although the deuterium reduction of an ethylenic linkage probably does not follow the above "*cis*" addition, the reduction of diethyl maleate should still be capable of yielding a different form from that given by diethyl fumarate. As shown by the constants (Table I), the diethyl succinic-α-d,α'-d specimens from both sources appeared to be identical, nor was the presence of isomers in either sample noticed during the distillation of the ester.

The densities of diethyl succinate-α-d,α'-d (Table I) from different reductions of the same material show some variance, possibly due to varying amounts of hydrogen "impurity." In a previous paper[1b] it was pointed out that the observed densities of dimethyl succinate-α-d_2,α'-d_2 and succinic-α-d_2,α'-d_2 anhydride were lower than and did not agree with the calculated values. The calculation of these values was based primarily upon the assumption of identical molecular volumes for deuterium and hydrogen. Since that time it has been observed[5] that the molecular volumes of the two isotopes are not identical and may differ sufficiently to affect the densities of deuterium compounds. However, it is evident that this effect must vary with the substances in question, as the densities[6] of several deuterium compounds, of established purity, agree very well with the calculated values; others show less agreement. In any case, it is worth mentioning that the densities (Tables I, II) observed for diethyl succinic-α-d,α'-d and its derivatives show fair agreement with the theoretical values. It is entirely probable that the discrepancy which does exist may be due both to a difference in molecular volumes and to hydrogen "impurities."

Succinic-α-d,α'-d acid was prepared by the hydrolysis of the ester from both of the abovementioned sources. These specimens of dideu-

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[1] (a) This is a portion of a thesis submitted in fulfilment of partial requirements for the degree of Doctor of Philosophy in Chemistry: (b) for previous paper in this field see McLean and Adams, THIS JOURNAL, **58**, 804 (1936).

A description of the investigation herewith reported was included in an address in connection with the Willard Gibbs Medal award to the senior author, May 23, 1936.

[2] After the preparation of this manuscript, an article by Biilmann, Jensen and Knuth, *Ber.*, **69**, 1031 (1936), reports the preparation of a deuterio camphane derivative which must be optically active due to the —CHD group. This paper will be discussed in a subsequent communication.

[3] Schoenheimer and Rittenberg, *J. Biol. Chem.*, **111**, 183 (1935).

[4] Erlenmeyer and Gärtner, *Helv. Chim. Acta*, **19**, 145, 331 (1936).

[5] Brickwedde and Teal, *Rev. Mod. Phys.*, **7**, 34 (1935).

[6] Erlenmeyer, Lobeck, Gärtner and Epprecht, *Helv. Chim. Acta*, **19**, 336 (1936); Bowman, Benedict and Taylor, THIS JOURNAL, **57**, 960 (1935); Breuer, *ibid.*, **57**, 2236 (1935).