[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Synthesis, Acidity and Decarboxylation of Substituted Mesitoic Acids[1]

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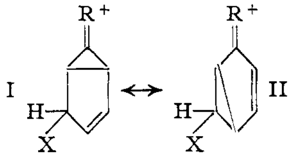
Mesitoic acid (2,4,6-trimethylbenzoic acid) and its 3-substituted nitro, bromo, chloro, hydroxy, amino, methyl and ethyl derivatives have been prepared. Their acidities in 55:45 ethanol–water have been measured and compared with those of the similarly substituted benzoic acids under the same conditions. The decarboxylation of mesitoic and hydroxymesitoic acid was studied both in 82.1% phosphoric acid and in 83.0% sulfuric acid, while the decarboxylation of methylmesitoic acid and of ethylmesitoic acid was studied only in the latter medium. Enthalpies, entropies and free energies of activation were calculated for the decarboxylations from the change of the rates with temperature.

It has long been established[2] that electron-releasing groups, such as the methyl, hydroxyl and methoxyl groups, are overwhelmingly ortho- and para-directing for entering electrophilic groups in aromatic substitution reactions. The low energy of activation of such reactions has been attributed to the stabilization of the activated complex by the now familiar ortho and para quinoidal forms.[3]

The effect of electron-releasing groups on electrophilic attack in the meta position has been less intensively studied. From investigation of the bromination of methyl *p*-tolyl ether and *p*-dimethoxybenzene de la Mare and Vernon[4] concluded that the methyl group was only weakly meta-activating, while the methoxyl group was even less effective. As a measure of the effect of the methyl group in toluene on meta-nitration Ingold, Lapworth, Rothstein and Ward assigned a "partial rate factor" of three.[5] Cleavage of unsymmetrical organomercury compounds with acids indicated to Kharasch and Flenner[6] that the *m*-tolyl radical was only slightly more electronegative than the phenyl radical. Similarly, it has been shown that a *m*-tolyl group will migrate somewhat more readily than a phenyl group in the acid-catalyzed rearrangement of a symmetrical pinacol to a pinacolone.[7] The present authors are not aware of any study of the effect of a meta-hydroxyl group on electrophilic attack.

The aim of this work was to obtain data on the effects on rates of electrophilic attack of methyl, ethyl and hydroxyl groups in meta positions and to interpret these data in terms of the thermodynamic functions of activation. It was hoped that the results would help to evaluate the contributions of meta-bonded structures such as I and II to the state of the activated complex during electrophilic attack.[8]



To avoid the complications of competitive reactions and of systems in which predominant attack occurs at the ortho and para positions, the decarboxylation of mesitoic acid (2,4,6-trimethylbenzoic acid) and its derivatives in sulfuric acid and in phosphoric acid was chosen as Schubert[9] had shown that it was a pseudo first-order reaction[10] conveniently followed by carbon dioxide evolution. Studies of the acid-catalyzed decarboxylations of a number of other aromatic or unsaturated acids have recently been reported: anthracene-9-carboxylic acid,[11] cinnamic acid and its α- and β-alkyl- and aryl-substituted derivatives,[12] salicylic acid,[13] 2,4-dihydroxybenzoic acid[13] and 2,4,6-trihydroxybenzoic acid.[13,14]

Mesitoic acid[15] and its 3-methyl[16] and 3-ethyl[17,18] derivatives were prepared by carbonation of the corresponding arylmagnesium bromides. 3-Bromo[19] and 3-nitromesitoic acid[20] were made by direct substitution. 3-Aminomesitoic acid, obtained by hydrogenation of the nitro acid, gave by way of its diazonium salts 3-chloro- and 3-hydroxymesitoic acids.

Table I summarizes the pK_a's for the mesitoic acids and for the similarly substituted benzoic acids in 55:45 ethanol–water at 22°. The pK_a's of the mesitoic acids are smaller than those of the corre-

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[1] This paper is taken from a dissertation submitted by Seymour Sands in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1953, and was presented at the Metropolitan-Long Island Meeting-in-Miniature of the American Chemical Society, February 20, 1953.

(2) A. F. Holleman, *Chem. Revs.*, **1**, 187 (1925).

(3) For example, G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 470ff.

(4) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951).

(5) C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *ibid.*, 1959 (1931). "Partial rate factor" is defined as the factor by which the introduction of a directing group increases the probability of substitution of a given atom under the conditions of comparison during a small element of time.

(6) M. S. Kharasch and A. L. Flenner, THIS JOURNAL, **54**, 674 (1932).

(7) W. E. Bachmann and H. R. Sternberger, *ibid.*, **56**, 170 (1934).

(8) Structures similar to I and II have recently been used to explain the effect of a meta-methoxyl group in the cationic polymerization of substituted styrenes: C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor and T. Alfrey, Jr., *ibid.*, **74**, 4848 (1952).

(9) W. M. Schubert, *ibid.*, **71**, 2639 (1949).

(10) For a detailed analysis of the kinetics and acid–base equilibria involved in the decarboxylation of mesitoic acid see R. Lantz, *Bull. soc. chim. France*, 1253 (1950).

(11) H. Schenkel, *Helv. Chim. Acta*, **29**, 436 (1946); H. Schenkel and M. Schenkel-Rudin, *ibid.*, **31**, 514 (1948).

(12) W. S. Johnson and W. E. Heinz, THIS JOURNAL, **71**, 2913 (1949).

(13) B. R. Brown, D. L. Hammick and A. J. B. Scholefield, *J. Chem. Soc.*, 778 (1950).

(14) B. R. Brown, W. W. Elliott and D. L. Hammick, *ibid.*, 1384 (1951).

(15) R. P. Barnes, *Org. Syntheses*, **21**, 78 (1941).

(16) L. I. Smith and C. L. Moyle, THIS JOURNAL, **55**, 1681 (1933).

(17) L. I. Smith and M. A. Kiess, *ibid.*, **61**, 284 (1939).

(18) M. Crawford and F. H. C. Stewart, *J. Chem. Soc.*, 4443 (1952).

(19) P. R. Schildneck and R. Adams, THIS JOURNAL, **53**, 343 (1931).

(20) F. W. Kuster and A. Stallberg, *Ann.*, **278**, 216 (1894).

sponding benzoic acids by 0.34–0.54 unit (column V). The smaller differences are found with those substituents whose coplanarity with the ring might be inhibited by adjacent methyl groups. The observation that the meta-hydroxyl group decreases the acidity of benzoic acid while it leaves that of mesitoic acid unchanged might be explained in a similar manner.

TABLE I

pK_a'S IN 55:45 ETHANOL–WATER AT 22°[a]

	Mesitoic acids		Benzoic acids		
3-Subst.	pK_a I	$pK_a^H - pK_a$ II	pK_a III	$pK_a^H - pK_a$ IV	III-I V
Nitro	4.34	0.98	4.76	1.07	0.42
Bromo	4.84	.48	5.23	.60	.39
Chloro	4.84	.48	5.38	.45	.54
Hydroxyl	5.32	.00	5.66	.17	.34
Hydrogen	5.32	.00	5.83	.00	.51
Amino	5.39	− .07	5.88	− .05	.49
Methyl	5.40	− .08	5.87	− .04	.47
Ethyl	5.50	− .18	5.87	− .04	.35

[a] pK_a's were determined from the pH's at half-neutralization, with ionic strength 0.002. pK_a^H is the pK_a of the unsubstituted acid.

For the studies of decarboxylation the apparatus of Schubert[9] was duplicated. In 83% sulfuric acid mesitoic acid and its hydroxy, methyl and ethyl derivatives evolved carbon dioxide at convenient rates between 48 and 86°, while bromomesitoic acid and nitromesitoic acid were decarboxylated only above 140 and 170°, respectively, and were not further studied. The decarboxylation of aminomesitoic acid was not investigated. The decarboxylations of the reactive mesitoic acids were followed over temperature ranges as wide as were allowed by the rates of the reactions and the solubilities of the acids. Because of the difficulty of measuring an experimental V_∞, first-order rate constants were obtained by the method of Guggenheim.[21] The rate constants are given in Table II, and plots of log *k versus* $1/T$ are shown in Fig. 1.[22]

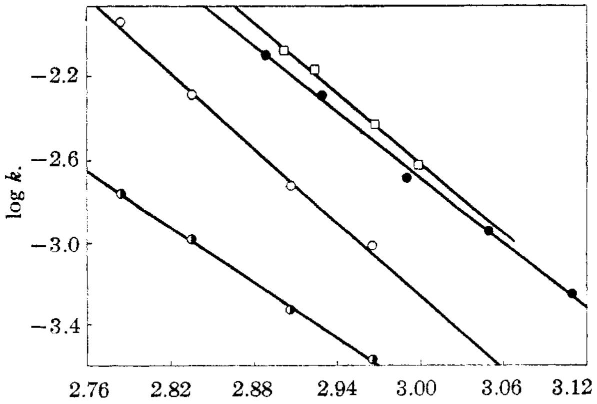

Fig. 1.—Decarboxylations in 83.0% sulfuric acid: ○, mesitoic acid; ●, methylmesitoic acid; □, 3-ethylmesitoic acid; ◐, 3-hydroxymesitoic acid.

TABLE II

RATES OF DECARBOXYLATIONS IN 83.0% SULFURIC ACID

3-Subst.	Temp., °C.	$k \times 10^3$ (sec.$^{-1}$)	Av. $k \times 10^3$
Hydrogen	64.2	0.938, 0.982, 1.00	0.974
	70.5	2.07, 1.83, 1.69	1.86
	79.2	5.22, 4.94, 5.22	5.13
	85.8	10.6, 12.1	11.4
Hydroxyl	64.2	0.278, 0.262	0.270
	70.5	0.494, 0.423, 0.456	0.456
	79.2	1.05, 1.05, 1.04	1.05
	85.8	1.76, 1.73, 1.73	1.74
Methyl	48.6	0.552, 0.566	0.559
	54.8	1.10, 1.13, 1.17	1.13
	61.4	2.27, 2.02	2.14
	68.5	5.35, 4.87	5.12
	73.2	7.95, 7.95	7.95
Ethyl	60.6	2.22, 2.64, 2.32	2.39
	64.0	3.59, 3.82	3.71
	69.0	6.56, 6.87, 6.82	6.74
	71.6	8.21, 7.86	8.04

The decarboxylations of mesitoic acid and hydroxymesitoic acid in 82.1% phosphoric acid were carried out between 103 and 135°. As an experimental V_∞ could be obtained in this medium, *k* was determined by the usual first-order plot of log V_∞ − log (V_∞ − *V*) *versus* time. Rate constants are given in Table III, and plots of log *k versus* $1/T$ are shown in Fig. 2.

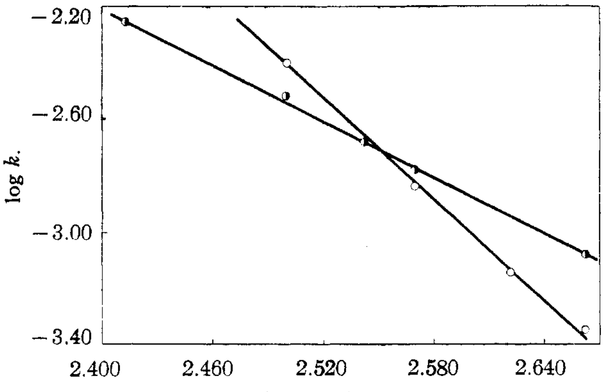

Fig. 2.—Decarboxylations in 82.1% phosphoric acid: ○, mesitoic acid; ◐, 3-hydroxymesitoic acid.

TABLE III

RATES OF DECARBOXYLATIONS IN 82.1% PHOSPHORIC ACID

3-Subst.	Temp., °C.	$k \times 10^3$ (sec.$^{-1}$)	Av. $k \times 10^3$
Hydrogen	103.6	0.433, 0.442, 0.469	0.448
	109.3	0.729, 0.706	0.717
	116.2	1.41, 1.37, 1.55	1.44
	127.0	4.00, 4.00, 3.92	3.97
Hydroxyl	103.6	0.812, 0.814, 0.873	0.833
	116.2	1.56, 1.69, 1.77	1.67
	120.4	2.04, 2.06, 2.14	2.08
	127.0	2.83, 3.12, 3.19	3.04
	134.9	5.63, 5.47, 5.73	5.58

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(21) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926). See also reference 13.

(22) The rate constants obtained for mesitoic acid in 83.0% sulfuric acid average about 13% higher than those reported for 83.3% sulfuric acid by Schubert,[9] with no trend with temperature. However, the energy of activation here reported (Table IV) agrees with that of Schubert, and no explanation for the slightly higher rates in the present work is suggested.

At 70° the relative rates of decarboxylation in sulfuric are: ethylmesitoic acid, 4.0; methylmesitoic acid, 3.2; mesitoic acid, 1.0; and hydroxymesitoic acid, 0.25. The more rapid reactions of the alkylmesitoic acids are in accord with the work cited on other electrophilic reactions,[4–7] while the slightly greater rate of ethyl- over methylmesitoic acid is of interest. At lower temperatures the ratio of the rates of each of the three substituted acids to that of mesitoic acid increases. From graphical extrapolations it is estimated that at temperatures below 30° the decarboxylation of hydroxymesitoic acid would be more rapid than that of mesitoic acid.

In phosphoric acid the rates of decarboxylations of mesitoic acid and its hydroxy derivative were the same at 119°. Hydroxymesitoic acid was the more reactive compound below this temperature but the less reactive above this temperature. Thus in terms of rates the present work does not allow classification of the meta-hydroxyl group as an activating or deactivating group in electrophilic attack without specification of conditions.

As for the effect of medium on the rates of decarboxylation, if values obtained by graphical extrapolation to 90° are used, it is found that the decarboxylation of mesitoic acid is about 160 times as fast in sulfuric acid as in phosphoric acid, while the corresponding ratio for the hydroxymesitoic acid is about 6.4.

The rate data were further analyzed by means of the Arrhenius equation

$$\ln k = \ln A - E/RT$$

and by the absolute rate equation.

$$\ln k/T = \ln R\kappa/Nh + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT$$

The transmission coefficient, κ, was set equal to unity. The calculated kinetic and thermodynamic functions are collected in Table IV.

TABLE IV

KINETIC AND THERMODYNAMIC FUNCTIONS FOR DECARBOXYLATIONS[a]

Medium	3-Subst.	log A	E	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta F^{\ddagger}$	$k \times 10^3$
Sulfuric acid, 83.0%	Hydrogen	15.0	27.7[b]	26.8	7.1	24.4[c]	1.78[c]
	Ethyl	14.4	25.9	24.8	3.8	23.5[c]	7.11[c]
	Methyl	13.9	23.7	23.3	−1.0	23.6[c]	5.61[c]
	Hydroxyl	10.3	21.3	20.8	−15.0	25.9[c]	0.44[c]
Phosphoric acid, 82.1%	Hydrogen	13.8	28.5	27.4	−1.3	27.9[c]	1.94[c]
	Hydroxyl	6.1	15.9	16.0	−30.1	27.8[c]	1.94[c]

[a] A and k are expressed in sec.$^{-1}$, E, $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$ in kcal. mole^{-1}, and $\Delta S^{\ddagger}$ in cal. mole^{-1} deg.$^{-1}$. Estimated average errors are: log A, 0.6; E and $\Delta H^{\ddagger}$, ±0.8; $\Delta S^{\ddagger}$, ±2.8; $\Delta F^{\ddagger}$, ±1.3. [b] A value of 27.4 kcal. mole^{-1} was reported by Schubert.[9] [c] The values for sulfuric acid and for phosphoric acid are for 70° and 119°, respectively.

The most striking feature of the data in Table IV is the decrease in log A, E, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as the 3-substituent becomes progessively more strongly electron-releasing in the sequence: hydrogen, ethyl, methyl and hydroxyl. The decarboxylation has been pictured[8–13] as an electrophilic attack in which a proton becomes attached to the 1-carbon bearing the carboxyl group, which departs as carbon dioxide and a proton attached to a base. In such an electrophilic attack the interaction of the electron-releasing group with the positively charged ring would decrease the enthalpy of activation and might be described by meta-bonded structures such as I and II.[23] With progressively more strongly electron-releasing groups on the 3-carbon, the contribution of such meta-bonded forms would become more important, and the bonds of the 1-carbon with the entering proton and with the departing carboxyl group would become more covalent and hence tetrahedrally directed. Such increasingly stringent geometric requirements for the activated complex would be expected to result in lowered entropies of activation, in accord with experimental findings. Finally, although substituents have a large effect on $\Delta H^{\ddagger}$ and on $\Delta S^{\ddagger}$, both $\Delta F^{\ddagger}$ and the rate of decarboxylation are relatively insensitive to changing electron-releasing substituents in the 3-position.

The analysis given above of parallel changes in enthalpies and entropies of activation is similar to the more general one of Hinshelwood.[24] Correlations of energy and entropy or steric factors have been made in other studies of decarboxylations.[13,25]

Acknowledgment.—The authors are glad to acknowledge several suggestions by Professor Frank C. Collins which aided greatly in the preparation of this manuscript.

Experimental[26]

Substituted Mesitoic and Benzoic Acids. 3-Nitromesitoic Acid.—To a well-stirred solution of 3.28 g. (20 mmoles) of mesitoic acid[15] in 400 ml. of sulfuric acid cooled in an ice-bath there was added 14.4 ml. of a solution of 2 ml. of nitric acid in 20 ml. of sulfuric acid. After complete addition the ice-bath was removed, and the mixture was stirred for 15 minutes. Pouring the reaction mixture on 500 g. of ice gave a solid which was crystallized twice from 50% ethanol to give 3.50 g. (16.7 mmoles, 84%) of 3-nitromesitoic acid, m.p. 180–182°; lit.[20] 182°.

Anal. Calcd. for $C_{10}H_{11}NO_4$: N, 7.00; neut. equiv., 209.2. Found: N, 7.40; neut. equiv., 210.0.

Contrary to a previous report[20] it was not found possible to prepare this acid by the hydrolysis of nitromesitonitrile with hot concentrated hydrochloric or sulfuric acids or with potassium hydroxide in ethylene glycol.

3-Aminomesitoic Acid.—A solution of 8.3 g. (40 mmoles) of 3-nitromesitoic acid in 100 ml. of ethanol containing 0.3 g. of Raney nickel catalyst was shaken with hydrogen under low pressure until uptake ceased. After removal of catalyst from the warmed reaction mixture cooling gave colorless crystals, which were recrystallized from 10% ethanol to give 7.0 (39.1 mmoles, 97%) of 3-aminomesitoic acid, m.p. 209–210° with charring beginning at 207°.

Anal. Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.30; N, 7.82. Found: C, 66.93; H, 7.41; N, 8.05.

The S-benzylthiouronium salt of 3-aminomesitoic acid melted at 178.5–179°.

Anal. Calcd. for $C_{18}H_{23}N_3O_2S$: N, 12.2. Found: N, 12.0.

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[23] Johnson and Heinz considered analogous positively charged structures as intermediates rather than as activated complexes in the decarboxylations of cinnamic acids.[12] This alternative point of view would not greatly alter the analysis given here as the formation of positively charged intermediates would proceed through transition states, whose energy would be affected by the factors discussed.

[24] C. N. Hinshelwood, "The Kinetics of Chemical Change," Clarendon Press, Oxford, 1940, p. 257.

[25] A. L. Bernoulli and W. Wege, *Helv. Chim. Acta*, **2**, 511 (1919); R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938); N. H. Cantwell and E. V. Brown, THIS JOURNAL, **74**, 5967 (1952).

[26] Melting points were taken with a modified Hershberg apparatus and are not further corrected. Boiling points are uncorrected. Microanalyses were performed by Drs. Weiler and Strauss, 164 Banbury Road, Oxford, England.

3-Hydroxymesitoic Acid.[27]—To a cold solution of 10.8 g. (60 mmoles) of 3-aminomesitoic acid and 6.0 ml. of sulfuric acid in 60 ml. of water a solution of 4.14 g. of sodium nitrite in 12 ml. of water was added dropwise with stirring. The resulting diazonium salt solution was added with stirring to 125 ml. of 20% sulfuric acid at 100°. Crystals from the cooled reaction mixture were recrystallized twice from water (activated carbon) to give 6.1 g. (31.6 mmoles, 56%) of colorless 3-hydroxymesitoic acid, m.p. 136.5–137.5°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; neut. equiv., 180.2. Found: C, 66.80; H, 6.55; neut. equiv., 180.6.

The α-naphthylurethan of 3-hydroxymesitoic acid melted at 204–205°.

Anal. Calcd. for $C_{21}H_{19}NO_4$: N, 4.01. Found: N, 4.12.

3-Chloromesitoic Acid.—To 10 ml. of concd. hydrochloric acid containing 3.6 g. (20 mmoles) of aminomesitoic acid there was added 1.5 g. (22 mmoles) of sodium nitrite dissolved in 10 ml. of water. This solution was cooled to 0° and was added with stirring to a similarly cooled solution containing a slight excess of cuprous chloride. The mixture was warmed on a steam-bath until gas evolution ceased. The solid formed was recrystallized from water–ethanol, giving 1.2 g. (6 mmoles, 30%) of 3-chloromesitoic acid as colorless crystals, m.p. 143.5–144.0°.

Anal. Calcd. for $C_{10}H_{11}O_2Cl$: Cl, 17.9; neut. equiv., 198.7. Found: Cl, 17.9; neut. equiv., 199.2.

3-Bromomesitoic Acid.—A solution of 2.5 g. (15 mmoles) of mesitoic acid in 35 ml. of glacial acetic acid was brominated with a solution of 2.4 g. (0.015 mole) of bromine in 10 ml. of glacial acetic acid. The reaction mixture was poured into 200 ml. of water, and the solid obtained was crystallized from water–ethanol to give 2.2 g. (9 mmoles, 60%) of 3-bromomesitoic acid as colorless crystals, m.p. 163.5° (lit.[19] 168°), neut. equiv., 242.8 (theoretical, 243.1).

3-Methyl- and 3-Ethylmesitoic Acid.—Isodurene (1,2,3,5-tetramethylbenzene) and ethylmesitylene, prepared by the reactions of mesitylmagnesium bromide with dimethyl sulfate and diethyl sulfate, were converted to their monobromo derivatives. Carbonation[15] of isodurylmagnesium bromide gave 3-methylmesitoic acid (2,3,4,6-tetramethylbenzoic acid), m.p. 164–165°, after three crystallizations from ethanol (lit.[28] 163–164°), neut. equiv., 178.1 (theoretical 178.2).

Carbonation of the Grignard reagent from 3-ethylbromomesitylene gave 3-ethylmesitoic acid (3-ethyl-2,4,6-trimethylbenzoic acid), m.p. 145–146°, after three crystallizations from ethanol–hexane.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39; neut. equiv., 192.3. Found: C, 74.76; H, 8.25; neut. equiv., 193.0.

The S-benzylthiouronium salt of 3-ethylmesitoic acid melted at 164.5°.

Anal. Calcd. for $C_{20}H_{26}N_2O_2S$: N, 7.9. Found: N, 7.7.

The 3-Substituted Benzoic Acids.—The 3-substituted nitro-, bromo-, chloro-, methyl- and aminobenzoic acids were obtained from Eastman Kodak Co., and after recrystallization had melting points in accord with those in the literature. 3-Hydroxybenzoic acid was prepared from diazotized 3-aminobenzoic acid and had a m.p. of 201–201.5°; lit.[29] 201°. 3-Ethylbenzoic acid was prepared from 2-ethylaniline by the sequence of Crawford and Stewart[18] and had a m.p. of 45°; lit.[18] 45°.

Determination of pK_a's.—pK_a's at 22° were determined from the pH's of half-neutralization[30] of 0.2 mmole of acid in 100 ml. of 55:45 ethanol–water, measured with a Beckman pH meter and using the equation

$$pK_a = pH_a - \log f_{A^-}$$

The dielectric constant was taken as 50, and the ionic strength was calculated as 0.002.

Decarboxylation of Mesitoic Acids. Apparatus and Procedure.—The apparatus and general decarboxylation procedure was that of Schubert.[9] Water saturated with carbon dioxide was used in the gas burets, and carbon dioxide covered all water surfaces exposed to the atmosphere.

Between 0.5 and 1.5 mmoles of organic acid was used with 10 ml. of sulfuric or phosphoric acid. As the volume increase following addition of the preheated acid was at a maximum in one to two minutes after the addition, zero time was taken as two minutes after the addition.

Determination of Rate Constants.—In sulfuric acid it was difficult to get a satisfactory V_∞, due perhaps to the slow evolution of sulfur dioxide. To avoid this uncertainty associated with long reaction times, the method of Guggenheim[21] was used. The results are summarized in Table II.

In phosphoric acid an experimental V_∞ could be obtained allowing use of the usual first-order plot of log V_∞ − log ($V_\infty - V$) *versus* time. The results are summarized in Table III.

Products.—Schubert has already demonstrated that mesitylene is formed from mesitoic acid in sulfuric acid,[9] and we have shown the same in phosphoric acid. The mesitylene isolated checked as to physical constants and gave trinitromesitylene, m.p. 228–230°, no depression on admixture with an authentic sample. Also, 3-hydroxymesitoic acid gave in phosphoric acid mesitol, m.p. 71–72°, no depression on admixture with an authentic sample.

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[27] No 3-hydroxymesitoic acid was obtained by treating 3-bromomesitol with *n*-butyllithium and then with carbon dioxide following the directions for *m*-hydroxybenzoic acid: S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **16**, 13 (1951).

[28] L. Gattermann, *Ber.*, **32**, 1118 (1899).

[29] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 225.

[30] This method is discussed by A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Part II, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1744.