measured activation energy will therefore not contain any ΔH of ionization of the aldehyde, if $BH^{\oplus}$ or $BH^{\oplus\prime}$ is the reactive species. On the other hand, if B is the reactive species, the ΔH of ionization will be incorporated in E_A but is probably not much different for the three aldehydes since they have nearly the same basicity. In any event, the change in values of the various k_1 or k_{1j} in going from one aldehyde to the next will depend on changes in structure. In so far as the large differences in activation energy can be interpreted in terms of the structure of the aldehyde, the following may be concluded: the decrease in activation energy in progressing from the trimethyl to the triisopropyl aldehyde can be attributed to a raising of the ground state energy of the reacting aldehyde or its conjugate acid as compared to the transition state (the transition state being near or at the hybrid structure IV). The higher energy of the ground state as compared to the transition state as the bulk of R increases would be due to greater resonance inhibition in III, or II (R interfering with coplanarity of

formyl) as compared to IV (R not sterically interfering with the resonance distribution of the positive charge).

The activation entropies in 85% sulfuric acid appear to be reflecting one or both of the following: (1) the participation to differing extents of different solvent species in the decarbonylation of the three aldehydes (a conclusion previously reached on the basis of the effect of changing medium on k_{obsd}) and (2) a greater rigidity of the transition state, as compared to the ground state, with increased bulk of R.

If the values of $\Delta S\ddagger$ (and E_A to some extent) reflect the extent of participation of various solvent species it would be of interest to determine these values with a particular aldehyde as a function of changing medium, e.g., changing sulfuric acid percentage. This also might be useful as a method of assessing the unimolecularity of a reaction for which the sum of the Hammett equation 6 is a constant.
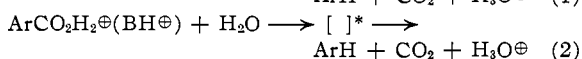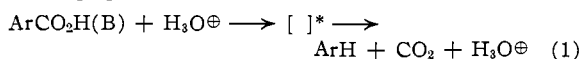
SEATTLE, WASH.

Aromatic Electrophilic Substitution by Hydrogen. IV. The Mechanism of the Acid-catalyzed Decarboxylation of Aromatic Acids[1]

BY W. M. SCHUBERT, JERE DONOHUE AND J. D. GARDNER

The rates of decarboxylation of five 2,4,6-trialkylbenzoic acids in strong sulfuric acid were determined. The degree of ionization of some of these acids to the conjugate acid and to the acylonium ion was determined spectroscopically. The data indicate the decarboxylation does not occur by the Hammett unimolecular mechanism. Catalysis by molecular sulfuric acid is the predominant process in greater than 80% sulfuric acid. General acid catalysis cannot be ruled out, since below 80% sulfuric acid the participation of oxonium ion catalysis appears to be discernible. Taking into account preliminary and side equilibria, the activating effect of p-methyl, ethyl or isopropyl is approximately the same. On the other hand, 2,4,6-triisopropylbenzoic acid decarboxylates much faster than 2,4,6-triethylbenzoic acid, and the latter faster than mesitoic acid. This is explained in terms of a steric inhibition of resonance factor.

In a previous study on the kinetics of the decarboxylation of mesitoic acid in 82–100% sulfuric acid at 80°,[2] the conclusion was reached that the reaction does not proceed by the Hammett unimolecular reaction path: $BH^{\oplus} \rightarrow$ Products. It also was concluded that the reaction occurs by specific oxonium ion catalysis, according to equation 1 or 2. These conclusions were based on the change in k_{obsd} with percentage sulfuric acid which shows a maximum at about monohydrate strength (Fig. 3), in which strength $[H_3O^{\oplus}]$ would be expected to be at a maximum. It was assumed that the decline in rate in greater than 85% sulfuric acid was due mainly to a decline in $[H_3O^{\oplus}]$, with some of the decline the result of reversible ionization to the acylonium ion, $ArCO^{\oplus}$. Furthermore, in deriving the rate expression 3, the tacit assumption that ionization to $ArCO_2H_2^{\oplus}$ is small was made.

$$ArCO_2H(B) + H_3O^{\oplus} \longrightarrow [\ ]^* \longrightarrow$$
$$ArH + CO_2 + H_3O^{\oplus} \quad (1)$$
$$ArCO_2H_2^{\oplus}(BH^{\oplus}) + H_2O \longrightarrow [\ ]^* \longrightarrow$$
$$ArH + CO_2 + H_3O^{\oplus} \quad (2)$$
$$k = \text{const }[H_3O^{\oplus}]; \text{ assume } f_B f_{H_3O^{\oplus}}/f_{tr}^{\oplus} = \text{constant} \quad (3)$$

In the present work, the actual degree of ionization of the mesitoic acid to $ArCO_2H_2^{\oplus}$ and to $ArCO^{\oplus}$ has been measured and correlated with rate data at 60°. With a view to determine the activating effect of p-alkyl the rates of decarboxylation of 2,6-dimethyl-4-ethylbenzoic acid and 2,6-dimethyl-4-isopropylbenzoic acid were also determined. In addition, the rates of decarboxylation of 2,4,6-triethyl- and 2,4,6-triisopropylbenzoic acids were measured to ascertain whether such steric factors as previously suggested[2] could be operative.

Experimental

2,6-Dimethyl-4-ethylbenzoic Acid.—A total of 134 g. (1.11 moles) of 2,6-xylidine (Eastman Kodak white label) was heated with absolute ethanol (84 g., 1.8 moles) and dry zinc chloride (151 g., 1.11 moles) in five separate Carius tubes at 270–280° for 12 hours. The resulting solid mass was decomposed by the addition of 10% HCl and the dark oily layer extracted with chloroform. The washed and dried chloroform extract was distilled through a modified Claisen head. The 70-g. fraction boiling at 129–137° (15–16 mm.) was carefully refractionated through a 23 in. twisted wire gauze column. The portion (27 g.) boiling at 104.5–105° (10 mm.), $n^{25}D$ 1.5404 was analyzed.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.50; H, 10.13. Found: C, 80.25; H, 10.13.

The above amine (30 g.) was treated by a method used to

(1) Supported in part by the Office of Naval Research.

(2) (a) W. M. Schubert, THIS JOURNAL, **71**, 2639 (1949); (b) W. M. Schubert and H. K. Latourette, *ibid.*, **74**, 1829 (1952).

convert o-toluidine to o-bromotoluene.[3] The crude product (16 g.) was fractionally distilled through the twisted wire gauze column to give 12.9 g. of colorless liquid, b.p. 103–104.5° (8–9 mm.), n^{25}D 1.5435.

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.35; H, 6.15; Br, 37.50. Found: C, 56.47; H, 6.45; Br, 37.07.

The bromo compound was converted to the Grignard reagent and carbonated by the method of Barnes,[4] except that an equimolar amount of ethyl bromide and two molar equivalents of magnesium were used. The crude acid (6.2 g.) was recrystallized twice from pentane to yield 3.0 g., m.p. 119–120°, of 2,6-dimethyl-4-ethylbenzoic acid.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.22; H, 8.03.

Gattermann[5] reported a m.p. of 101° for 2,6-dimethyl-4-ethylbenzoic acid obtained by hydrolysis of the nitrile prepared by the reaction of 1,3-dimethyl-5-ethylbenzene with cyanogen chloride and aluminum chloride. In these laboratories, an acid was prepared from 1,3-dimethyl-5-ethylbenzene by bromination[6] followed by carbonation of the Grignard reagent of the bromo hydrocarbon. Upon repeated recrystallization, the acid gave a m.p. of 102–104°; when mixed with the 119–120° melting acid, it melted at 107–109°. It is concluded Gattermann's acid and the acid melting at 102–104° must contain some of the isomeric 2,4-dimethyl-6-ethylbenzoic acid which is difficult to remove by crystallization.

Decarboxylation of 2,6-Dimethyl-4-ethylbenzoic Acid and Oxidation of the Corresponding Hydrocarbon.—The carboxylic acid (2.8 g.) of m.p. 119–120° was heated with 20 ml. of 85% sulfuric acid for three hours. The mixture was cooled, diluted with water and extracted with petroleum ether. The petroleum ether extract was washed, dried and distilled in a modified Claisen flask. After distillation of the petroleum ether a very small forerun and then the main fraction was obtained; yield 0.76 g. (36%), b.p. 176–177°, d^{25} 0.8466, n^{23}D 1.4959.

The hydrocarbon (0.70 g.) was heated two days with 6.9 g. of potassium permanganate in 100 ml. of water, yielding 0.25 g. (25%) of trimesic acid, m.p. 362–365°, no depression with authentic trimesic acid. The methyl ester melted at 143–144° and gave no depression in m.p. with authentic methyl ester of trimesic acid.

2,6-Dimethyl-4-isopropylbenzoic Acid.—This was prepared by the same procedure used for 2,6-dimethyl-4-ethylbenzoic acid; a mixture of 2,6-xylidine (105 g., 0.87 mole), isopropyl alcohol (78 g., 1.3 moles) and anhydrous zinc chloride 150 g., 1.1 moles) at 270–280° for 12 hours yielded 45 g., b.p. 112–113° (8 mm.) in twisted wire gauze column, n^{25}D 1.5329.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50. Found: C, 80.85; H, 10.31.

The amine (51 g., 0.31 mole) gave 40 g. of 1-bromo-2,6-dimethyl-4-isopropylbenzene, b.p. 113–123°. A portion of this (17 g.) when fractionated through the twisted wire gauze column gave 9.1 g., b.p. 110–111° (9 mm.), n^{25}D 1.5367.

Anal. Calcd. for $C_{11}H_{15}Br$: C, 58.16; H, 6.66; Br, 35.18. Found: C, 58.20; H, 6.89; Br, 35.02.

The bromo hydrocarbon (15 g.) gave 8.5 g. of crude 2,6-dimethyl-4-isopropylbenzoic acid, m.p. 109–115°. Repeated recrystallization from pentane gave 3.4 g., m.p. 117–118°.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.85; H, 8.10.

Decarboxylation of 2,6-Dimethyl-4-isopropylbenzoic Acid and Oxidation of the Corresponding Hydrocarbon.—The acid (2.6 g.) was heated with 83% sulfuric acid (20 ml.) for 8 hours. The hydrocarbon was isolated and purified as was 1,3-dimethyl-5-ethylbenzene. There was obtained a small forerun, b.p. 178–186°, followed by the main fraction, b.p. 186–188°, yield 0.67 g. (41%), d^{25} 0.8598, n^{25}D 1.4922.

Oxidation of the 1,3-dimethyl-5-isopropylbenzene with aqueous permanganate was incomplete, probably because of the resistance of the isopropyl group to oxidation. The

hydrocarbon (0.60 g.) was then oxidized with nitric acid by the method used on mesitylene.[7] The yield was 0.10 g. (16.4%) of 3,5-dimethylbenzoic acid, m.p. 161–162°, no depression with an authentic sample prepared from mesitylene.

Preparation of Other Materials.—The carbonation method used in the final step of preparing the above acids was used to make the known 2,4,6-triethylbenzoic acid,[8] m.p. 113–113.5° and 2,4,6-triisopropylbenzoic acid[9] m.p. 184–185°.

Sulfuric acid solutions were prepared and their strength determined as before.[2]

Kinetic Method.—A gasometric and a spectrophotometric method were used. The gasometric method was run with approximately 0.05 to 0.1 M carboxylic acid solutions in 10 to 20 ml. of sulfuric acid in the apparatus previously described.[2] The only modification in the apparatus was that the leveling buret and manometer also were cooled by water at room temperature in addition to the gas cooler and gas collector. Failure to cool the leveling buret to the same temperature resulted in the escape of carbon dioxide through the aqueous solution to the warm side.

The spectrophotometric method, used on mesitoic acid at 60°, was exactly as described in the preceding article.[10] The carboxylic acid concentration was 10^{-5} M. The change in ultraviolet spectrum was followed at several wave lengths in the interval from 270 to 300 mμ.

Kinetic Results.—In Tables I and IV are listed values of the first-order rate constant obtained with each alkylbenzoic acid studied. The gasometric rate constants were calculated from the slope of the best straight line obtained in a plot of log ($V_\infty - V$) against time. The gasometric rate constants obtained in the faster runs and in concentrations of sulfuric acid in which no hydrocarbon layer separated are considered fairly reliable. A layer was noticeable only in the case of mesitoic acid, 2,6-dimethyl-4-ethylbenzoic acid and 2,6-dimethyl-4-isopropylbenzoic acid in concentrations of sulfuric acid below about 84%. The rate constants obtained in percentages of sulfuric acid in which a layer separated are probably somewhat low because of some partition of the acid into this small layer.[10] In slow runs there was a definite upward drift in calculated k values during an individual run, due probably to the slow loss of carbon dioxide from the gas collecting buret by solution into the level-

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECARBOXYLATION IN VARIOUS PERCENTAGES OF SULFURIC ACID

A. 2,6-Dimethyl-4-ethylbenzoic acid (I) and 2,6-dimethyl-4-isopropylbenzoic acid (II) at 80.0°; gasometric method

% H_2SO_4	$k \times 10^3$(sec.$^{-1}$) I	II
82.5	5.09, 5.02	4.03, 4.01
84.9	5.46, 5.31	5.26, 5.28
87.5	5.15, 5.10	5.13, 5.13
90.1	4.09, 4.03	4.29, 4.17
93.1	2.63, 2.63	2.51, 2.54
96.0	0.85, 0.85	0.90, 0.88
100	0	0

B. 2,4,6-Triethylbenzoic acid (III) and 2,4,6-triisopropyl-benzoic acid (IV) at 60.0°; gasometric method

% H_2SO_4	$k \times 10^3$(sec.$^{-1}$) III	IV
88.7	1.86, 1.92	....
89.9	1.70, 1.76	....
91.4	1.34, 1.34	....
93.0	0.97, 0.95	3.10, 2.96
94.5	.55, .54	1.25, 1.24
96.0	.21, .22	0.55, 0.67
97.4	....	0.25, 0.27
100.1		

(3) L. A. Bigelow, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 135.

(4) R. P. Barnes, *Org. Syntheses*, **21**, 77 (1941).

(5) L. Gattermann, S. Fritz and K. Beck, *Ber.*, **32**, 1122 (1899).

(6) A. Töhl and A. Geyger, *Ber.*, **25**, 1533 (1892).

(7) H. R. Snyder, R. R. Adams and A. V. McIntosh, Jr., THIS JOURNAL, **63**, 3280 (1941).

(8) R. C. Fuson and J. Corse, *ibid.*, **60**, 2063 (1938).

(9) R. C. Fuson and E. C. Horning, *ibid.*, **62**, 2962 (1940).

(10) W. M. Schubert and R. E. Zahler, *ibid.*, **76**, 1 (1954).

TABLE II

VALUES OF ε × 10⁻³ AND pK_a FOR MESITOIC ACID AT ROOM TEMPERATURE

λ, mμ	ε × 10⁻³ in various % sulfuric acid										−pK_a	εBH⊕ × 10⁻³ calcd.
	70.3	80.3	84.9	90.2	91.2	93.7	96.0	97.0	98.6	100.0		
275	1.22	3.27	5.32	6.22	6.84	7.82	9.08	11.42	14.15	16.95	7.11 ± 0.02	6.64
280	1.00	3.02	5.42	6.77	7.57	8.98	10.53	13.62	17.22	20.00	7.26 ± .06	7.46
285	0.77	2.60	5.12	6.78	7.58	9.10	10.50	13.25	15.85	18.23	7.33 ± .04	7.47
290	.57	2.08	4.30	5.90	6.58	7.82	8.43	9.50	10.18	10.45	7.39 ± .04	6.73
295	.39	1.63	3.33	4.67	5.18	5.82	5.91	5.58	5.03	4.37	7.36 ± .05	5.12
300	.26	1.23	2.44	3.48	3.74	4.15	4.23	3.58	2.87	2.16	7.34 ± .08	3.82
340	.05	..	0.37	0.70	0.70	1.05	1.93	2.57	3.72	4.49	....	..

Av. 7.3

ing water and escape into the atmosphere above the water in the leveling buret.

Rate constants obtained in the spectrophotometric runs are considered more reliable[10] and showed no drifts in any percentage sulfuric acid.

Discussion

Ionization of the Trialkylbenzoic Acids. pK_a **Values.**—Two ionization equilibria need be considered for the trialkylbenzoic acid,[11] the equilibrium, equation 6, between the free carboxylic acid and its conjugate acid, and the equilibrium, equation 7, between the conjugate acid and the acylonium ion, Ac⊕.

In Fig. 1 are plotted some of the ultraviolet spectra determined for mesitoic acid at room temperature in several concentrations of sulfuric acid. The spectrum in 70% sulfuric acid is assumed to be that of the free carboxylic acid. As the concentration of sulfuric acid is raised a peak at 280 mμ begins to appear, presumably the peak for the conjugate acid, BH⊕. The changes in absorption spectra up to about 91% sulfuric acid are qualitatively what would be expected for the equilibrium of equation 6 with the ionization to BH⊕ complete at about 91% sulfuric acid. However, in greater than 91% sulfuric acid there is a sudden very marked increase in absorption at 270–290 mμ which reaches a maximum in 100% sulfuric acid. Furthermore, a new small peak begins to appear in about 93% sulfuric acid at 340 mμ and reaches a maximum in 100% sulfuric acid. The spectrum in 100% sulfuric acid is assumed to be that of the acylonium ion. Mesitoic acid was shown by cryoscopic measurements of Hammett and Treffers to be ionized practically completely to acylonium ion in 100% sulfuric acid.[11] The appearance of the spectra of Fig. 1 suggests the concentration of acylonium ion can safely be assumed to be negligible in 90.2%. With this assumption, the pK_a of mesitoic acid was determined by the Hammett method.[12]

$$K_a + \epsilon_{BH\oplus}\left(\frac{h_0}{\epsilon_B - \epsilon}\right) - \frac{h_0\epsilon}{\epsilon_B - \epsilon} = 0 \qquad (4)$$

Equation 4 was solved at each of several wave lengths by the method of least squares using the absorption spectra in 80.3, 84.9 and 90.2% sulfuric acid. The wave lengths used are those in which the ϵ_B curve is relatively flat and hence the medium effects minimized. The calculated pK_a is −7.3. The pertinent data are summarized in Table II.

(11) L. P. Hammett and H. P. Treffers, THIS JOURNAL, **59**, 1708 (1937).

(12) L. A. Flexser, L. P. Hammett and A. Dingwall, ibid., **57**, 2103 (1935).

Solution of equation 4 also gave values for εBH⊕. It is interesting to note that the εBH⊕ calculated closely parallels the ε found in 91.2% sulfuric acid, in agreement with the assumption of negligible acylonium ion formation in this region.
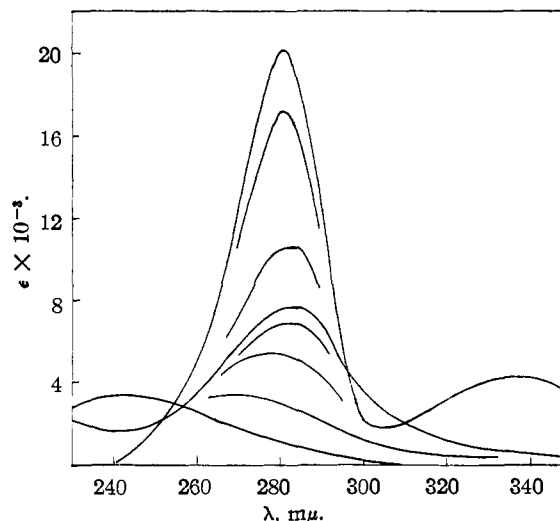

Fig. 1.—Spectra of mesitoic acid in various concentrations of H_2SO_4 at room temperature. Beginning with the curve giving the highest peak and working down, the percentages H_2SO_4 are: 100, 98.6, 96.0, 91.2, 90.2, 84.9, 80.3 and 70.3.

The same method was used to calculate the pK_a of mesitoic acid at 60° and gave a value of −7.4. In this case the spectra changed with time so that it was necessary to calculate the spectra at zero time from an extrapolation of the first-order plots of log $(D - D_\infty)$ vs. time. See Fig. 2 for the ϵ_0 plots.

At room temperature the pK_a values of 2,6-dimethyl-4-ethylbenzoic acid and 2,6-dimethyl-4-isopropylbenzoic acid were found identical within experimental error, −7.4. The pK_a values for 2,4,6-triethyl- and 2,4,6-triisopropylbenzoic acids were not determined.

Ionization to Acylonium Ion.—The ratio [BH⊕]/[Ac⊕] can be calculated from equation 5, if εBH⊕ and εAc⊕ are known, in media in which [B] is negligible. The degree of ionization of mesitoic acid conjugate acid to its acylonium ion was determined in this way.

$$\frac{[BH\oplus]}{[Ac\oplus]} = \frac{\epsilon_{Ac\oplus} - \epsilon}{\epsilon - \epsilon_{BH\oplus}} \qquad (5)$$
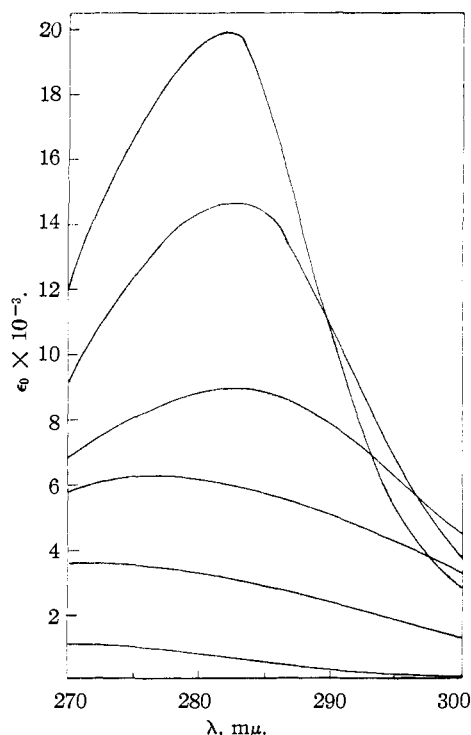
Assuming [B] negligible in 93.7, 96.0, 97.0 and

Fig. 2.—Zero time spectra of mesitoic acid in various concentrations of H_2SO_4 at 60°. Beginning with the uppermost curve and working down, the percentages of H_2SO_4 are: 100, 95.5, 90.3, 84.8, 80.5, 70.4.

98.6% sulfuric acid, $[BH^{\oplus}]/[Ac^{\oplus}]$ was solved for 280, 285 and 340 mμ wave lengths at which the $\epsilon_{BH^{\oplus}}$ curve is relatively flat. Values of $\epsilon_{BH^{\oplus}}$ were taken from ϵ in 91.2% sulfuric acid (which checks closely with $\epsilon_{BH^{\oplus}}$ calculated from equation 4) and $\epsilon_{Ac^{\oplus}}$ from ϵ in 100% sulfuric acid. Values of $[BH^{+}]/[Ac^{+}]$ obtained are given in Table III.

TABLE III

VALUES OF $[BH^{\oplus}]/[Ac^{\oplus}]$ AND $pK'_{BH^{\oplus}}$ FOR MESITOIC ACID AT ROOM TEMPERATURE

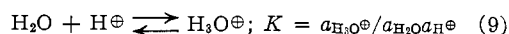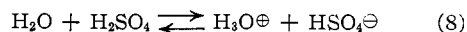| % H_2SO_4	$-H_0$	[H₂O] stoich.	$[BH^{\oplus}]/[Ac^{\oplus}]$ at various λ, mμ				$pK'_{BH^{\oplus}}$
			280	285	290	Av.	
93.7	8.95	6.41	7.82	6.01	9.83	7.89	9.03 ± 0.10
96.0	9.16	4.08	3.20	2.65	2.08	2.64	8.97 ± .10
97.0	9.60	3.06	1.05	0.88	1.03	0.99	9.10 ± .05
98.6	10.29	1.43	0.29	0.29	0.26	0.25	(9.56 ± .03)

Av. 9.1

A constant, $pK_{BH^{\oplus}}$, can be defined in terms of the equilibrium 7. This constant enables calculation of $[BH^{+}]/[Ac^{+}]$ at other acid concentrations and may be of use in quantitative comparisons of ionizations of the type of equation 7. The derivation of $pK_{BH^{\oplus}}$ is similar to that employed by Gold and Hawes for pK_{ROH}, defined for the equilibrium between the base C_6H_5COH and the ion $C_6H_5C^{\oplus}$.[13] In the triphenylcarbinol ionization, $[BH^{+}]$ is negligible, whereas in the mesitoic acid ionization, [B] is assumed negligible in the region in which $[Ac^{+}]$ is appreciable.

$$B + H^{\oplus} \rightleftarrows BH^{\oplus} \qquad (6)$$

$$BH^{\oplus} \rightleftarrows Ac^{\oplus} + H_2O \qquad (7)$$
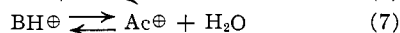
(13) V. Gold and B. W. V. Hawes, J. Chem. Soc., 2102 (1951).

$$H_2O + H_2SO_4 \rightleftarrows H_3O^{\oplus} + HSO_4^{\ominus} \qquad (8)$$

$$H_2O + H^{\oplus} \rightleftarrows H_3O^{\oplus}; \quad K = a_{H_3O^{\oplus}}/a_{H_2O}a_{H^{\oplus}} \qquad (9)$$

The equilibrium constant of equation 7 is

$$K_{BH^{\oplus}} = \frac{[Ac^{\oplus}]}{[BH^{\oplus}]} a_{H_2O} \frac{f_{Ac^{\ominus}}}{f_{BH^{\ominus}}} \qquad (10)$$

If, following Gold and Hawes,[13] the activity coefficient ratio $f_{Ac^{\ominus}}/f_{BH^{\ominus}}$ is assumed to be unity, then

$$pK_{BH^{\oplus}} = \log([BH^{+}]/[Ac^{+}]) - \log a_{H_2O} \qquad (11)$$

By use of the equilibrium constant for the formal equilibrium of equation 9, equation 10 can be converted to 12, where $h_0 = a_{H^{\oplus}}f_B/f_{BH^{\oplus}}$.

$$K_{BH^{\oplus}} K = K'_{BH^{\oplus}} = \frac{[Ac^{\oplus}][H_3O^{\oplus}]}{[BH^{\oplus}]h_0}\left(\frac{f_B f_{Ac^{\ominus}}f_{H_2O^{\oplus}}}{f_{BH^{\oplus}}f_{BH^{\ominus}}}\right) \qquad (12)$$

Again following Gold and Hawes,[13] the activity coefficient term is assumed a constant. The numerator and the denominator of this term have the same net charge and consist of the same structural elements. Then

$$pK'_{BH^{\oplus}} = \log([BH^{\oplus}]/[Ac^{\oplus}]) - H_0 - \log[H_3O^{\oplus}] \qquad (13)$$

Equation 11 is useful when a_{H_2O} is known. In the higher concentrations of sulfuric acid, in which a_{H_2O} is known with less certainty, equation 13 is more useful, since $[H_3O^{\oplus}]$ can be set equal to stoichiometric water concentration. With the aid of equation 13, values of $pK'_{BH^{\oplus}}$ were calculated from values of $[BH^{\oplus}]/[Ac^{\oplus}]$ given in Table III. The values of $pK'_{BH^{\oplus}}$ are shown in Table III and yield an average value of 9.1.

The Unimolecular Mechanism.—The experimental data on mesitoic acid are in wide disagreement with the Hammett unimolecular mechanism 14.

$$BH^{\oplus} \xrightarrow{k_2} CO_2 + ArH + H^{\oplus} \qquad (14)$$

$$v = k_2[BH^{+}]f_{BH^{+}}/f_{tr^{+}} \qquad (15)$$

The Brönsted rate equation 15 for reaction path 14 can easily be transformed into the equation in H_0, 16, or into equation 17, where $k'_2 = \text{const.} \times k_2$.[2b]

$$\log k_{obsd} + H_0 - \log\frac{[B]}{[B]_{stoich}} = \text{const.} \qquad (16)$$

$$k_{obsd} = \frac{v}{[B]_{stoich}} = \frac{k'_2[BH^{+}]}{[B] + [BH^{+}] + [Ac^{+}]},$$
$$\text{assuming } f_{BH^{+}}/f_{tr^{+}} = \text{const.} \qquad (17)$$

Equation 16 is more useful as a check of the unimolecular mechanism in media in which $[BH^{+}]$ is not too large, whereas 17 is more useful when $[BH^{+}]$ is large relative to [B]. In Table IV are listed values of the sum of equation 16 and of k'_2 of equation 17 in the various percentages of sulfuric acid in which k_{obsd} was determined by the spectrophotometric method. The relative concentrations of B, BH^{+} and Ac^{+} were calculated from the values of pK_a and $pK'_{BH^{+}}$ determined at room temperature. It is seen that the deviation from apparent unimolecular behavior as reflected in the sum of equation 16 is considerable, particularly in the region of appreciable ionization to BH^{+}. It is considered unlikely that the ratio $f_{BH^{+}}/f_{tr^{+}}$ should change so markedly as to account for the rapid change in k'_2 with percentage sulfuric acid. Nor is it likely that the ionization equilibria of equations 4

and 5 would change in such a marked manner between room temperature (temperature at which the ionization was measured) and 60° (temperature at which k_{obsd} was determined). Spectra at 60°, extrapolated to zero time, show the ionization equilibria not to be affected greatly by temperature (Fig. 2). From the ϵ_0 at 60°, pK_a was calculated to be -7.4. From ϵ_0 in 95.5% only, pK'_{BH^+} was calculated to be 8.4.

<div align="center">TABLE IV</div>

VALUES OF k_{obsd} (SPECTROPHOTOMETRIC) AND CHECK
AGAINST MECHANISM 14 AND 17

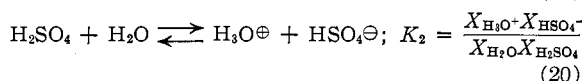| % H_2SO_4	k_{obsd}. $\times 10^4$, sec.$^{-1}$	[B]:[BH$^\oplus$]: [Ac$^\ominus$]	Sum eq. 16	k'_2 $\times 10^3$, sec.$^{-1}$	H_2SO_4	$k_{H_2SO_4}$
72.0	2.09, 2.06	100:3:0	-9.46	..	$0.206^{a,c}$	104^c
76.2	3.27	100:11:0	-9.75	..	$.336^{a,c}$	108^c
80.5	6.65, 6.70	100:39:0	-9.72	2.34	$.70^{a,c}$	133^c
84.8	7.30	51:100:0	-10.21	1.10	2.1^b	103
90.3	4.90	12:100:0	-10.57	0.55	$7.1^{b,d}$	64^d
95.5	2.5	2:100:45	.....	0.37	$13.3^{b,d}$	138^d

^{a} $K_2 = 50$ assumed for equilibrium 20.[15] ^{b} Ionization of equation 20 assumed complete.[14] ^{c} Subject to error because $K_2 > 50$. ^{d} Subject to large error because [B] small.

Bimolecular Mechanisms.—Although the conclusion that the Hammett unimolecular mechanism does not apply to the decarboxylation of mesitoic acid has been verified, it seems unlikely that the reaction occurs by specific oxonium ion catalysis (equation 1 or 2) as originally put forth.[2a] It is true that k_{obsd} is at a maximum in monohydrate strength sulfuric acid (84.5%), in which strength [H_3O^+] is probably at or near a maximum. However, it has been shown that a goodly portion of the leveling off in k_{obsd} in going from 80 to 85% sulfuric acid is attributable to appreciable ionization of the acid to $ArCO_2H_2^+$.

The possibility that specific molecular sulfuric acid catalysis occurs (process 17 or 18 in which $HA_i = H_2SO_4$) can be evaluated with the aid of the rate expression 19, if the concentration of molecular sulfuric acid is known.

$$B + HA_i \xrightarrow{k_i} \text{Products} \qquad (17)$$

$$BH^\oplus + A_i \longrightarrow \text{Products} \qquad (18)$$
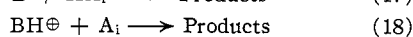
$$k_{H_2SO_4} = k_{obsd}\frac{[B] + [BH^\oplus]}{[B][H_2SO_4]}; \text{ assume } f_Bf_{H_2SO_4}/f_{tr} = \text{const.}$$
$$\qquad (19)$$

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^\oplus + HSO_4\ominus; \quad K_2 = \frac{X_{H_3O^+}X_{HSO_4^-}}{X_{H_2O}X_{H_2SO_4}}$$
$$\qquad (20)$$

This quantity was calculated for 90.3 and 95.5% sulfuric acid assuming as did Brand[14] that reaction 20 is complete in this region. In below 90% acid, [H_2SO_4] was calculated using a value of 50 for the mole fraction equilibrium constant of equation 20. It is assumed that this value is valid at the temperature of the kinetic runs, 60°. Deno and Taft[15] have shown the value 50 for K_2 to be valid in 83 to 89% acid but not below 85% sulfuric acid. Calculated values of $k_{H_2SO_4}$ in Table IV show a fair degree of constancy. However, two points should be borne in mind before a conclusion

(14) J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).
(15) N. C. Deno and R. W. Taft, Jr., THIS JOURNAL, **76**, 244 (1954). We are indebted to Dr. Taft for kindly furnishing us with a copy of the manuscript in advance of publication.

is made: (1) The values of $k_{H_2SO_4}$ in 90.3 and 95.5% sulfuric acid are subject to possible large error because [B] is small relative to [BH$^\oplus$] and/or [Ac$^\oplus$]. A slight error in pK_a and $pK'_{BH^\oplus}$ can lead to a large percentage error in calculating [B] (the percentage error in calculating [BH$^+$] would be less). (2) The assumption that $K_2 = 50$ is not valid in 80.5, 76.2 and 72.0% sulfuric acid. Rather, K_2 is thought to be increasing in this region.[15] A larger value of K_2 would make [H_2SO_4] smaller and $k_{H_2SO_4}$ greater than calculated. The value of K_2 would not have to increase tremendously in 80.5 to 72% sulfuric acid for $k_{H_2SO_4}$ to depart significantly from constancy. An increase in $k_{H_2SO_4}$ in this region would indicate catalysis by more than just molecular sulfuric acid, *i.e.*, by $H_3O^\oplus$ as well. Thus the only conclusion to be made from the test made of the rate equation 19 is that although molecular sulfuric acid catalysis must play a large role in any bimolecular mechanism, and probably highly predominates beyond 80% sulfuric acid, catalysis by other species cannot as yet be ruled out. The fact that there is still an appreciable rate in 72% sulfuric acid suggests that H_3O^+ catalysis may be becoming more prominent in this region.

Comparison of the Various Aromatic Acids.—In the decarboxylations of 2,6-dimethyl-4-ethylbenzoic acid and 2,6-dimethyl-4-isopropylbenzoic acid, whatever solvent acids, HA_i, or bases, A_i, that are participating must have very nearly the same relative effectiveness as in the decarboxylation of mesitoic acid. This is seen from the fact that (1) the curves obtained in the plot of k_{obsd} against percentage sulfuric acid for the three acids parallel each other closely (Fig. 3), and (2) the extent of the ionization equilibria 6 and 7 is about the same for each acid (*e.g.*, compare Figs. 1 and 4).

Only fragmentary curves for k_{obsd} *vs.* percentage sulfuric acid (Fig. 3) are given for the decarboxylation reaction of 2,4,6-triethyl- and 2,4,6-trisopropylbenzoic acids. Also, the degree of ionization of these acids has not been measured. Therefore any conclusions regarding the relative effectiveness of species HA_i or A_i in the decarbonylation of these acids are not warranted.

The rates of decarboxylation of mesitoic acid, 2,6-dimethyl-4-ethylbenzoic acid and 2,6-dimethyl-isopropylbenzoic acid at 80° do not differ appreciably in each concentration of sulfuric acid in which the reaction was studied. Since the degree of ionization according to equations 4 and 5 is approximately the same for each of the three acids, this suggests that the activating effect in the rate-controlling step is about equal for p-methyl, ethyl or isopropyl. Ignoring entropy effects, it would thus appear that the demands placed on the hyperconjugative influence of the p-alkyl are not much different in the ground state (formally, at least, the conjugate acid II) than in the transition state (at or near III, leaving out participating solvent species). However, one would expect that distribution of the plus charge would be sterically interfered with more in the conjugate acid II than in the transition state III. Although the activating effect of p-methyl, ethyl and isopropyl is about the same, a p-alkyl substituent does exert an activating
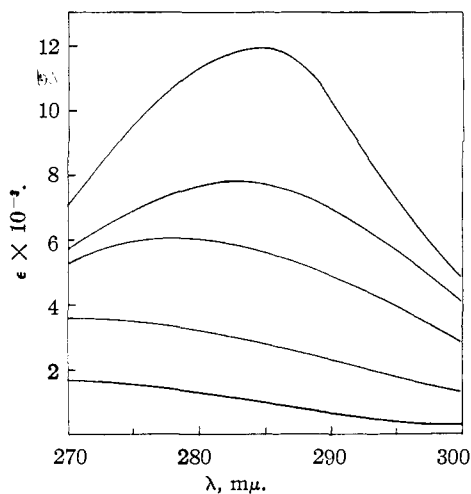
Fig. 3.—Spectra of 2,6-dimethyl-4-ethylbenzoic acid in various concentrations of H_2SO_4 at room temperature. Beginning with the uppermost curve and working down, the percentages of H_2SO_4 are: 96.1, 90.2, 85.3, 80.3, 70.3.
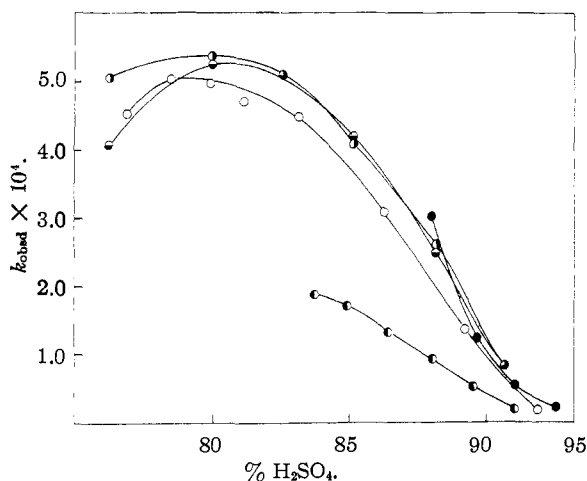

Fig. 4.—Change in k_{obsd} with $\%$ H_2SO_4: O, mesitoic acid at 80°[2]; ◑, 2,6-dimethyl-4-ethylbenzoic acid at 80°; ◒, 2,6-dimethyl-4-isopropylbenzoic acid at 80°; ◐, 2,4,6-triethylbenzoic acid at 60°; ●, 2,4,6-triisopropylbenzoic acid at 60°.

influence on the reaction. Thus 2,6-dimethylbenzoic acid fails to decarboxylate at a measurable rate at 100° in 85% sulfuric acid. Some of this in-

ertness may be due to a weaker basicity of the dimethylbenzoic acid.

If it is assumed that an o-isopropyl substituent cannot exert a greater activating effect than an o-ethyl or methyl substituent by its electron release tendencies alone, then the much greater rate of decarboxylation of 2,4,6-triisopropylbenzoic acid is probably attributable to a steric effect. Rate differences will of course arise merely as the result of differences in the ionization equilibria of equations 6 and 7 giving rise to different concentrations of the reactive species.[16] If the rate-controlling step involves the free base, B, then the considerably faster rate of decarboxylation of the triisopropyl acid *might* be attributable to its having a considerable weaker basicity, However, it is not thought likely that the triisopropyl acid is a much weaker base. On the other hand, if the rate-controlling step involves $BH^{\oplus}$ or another conjugate acid $B'H^{\oplus}$[10] it is highly unlikely that $[BH^+]$ is so many fold greater for the triisopropylbenzoic acid. Therefore, as in the decarbonylation of alkylbenzaldehydes, it is suggested that increasing bulk of the o-substituents serves to raise the ground state energy of the reacting species, I or II, by steric interference with the resonance interaction of the carbonyl group and the ring.[10] Resonance distribution of the plus charge in the transition state (at or near III) would appear not to be interfered with sterically.

I   II   III
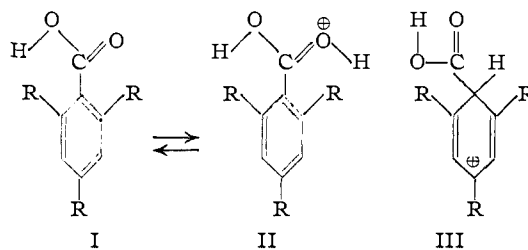
Seattle, Wash.

(16) Shortly after this manuscript was submitted there appeared an article by F. M. Beringer and S. Sands, This Journal, 75, 3319 (1953), dealing with the effect of m-substitution on the rate, heat of activation and entropy of activation of mesitoic acid decarboxylation in 83.0% sulfuric acid and 82.1% phosphoric acid. Since these authors did not consider or measure the effect of changes in preliminary or side equilibria (e.g., equations 6 or 7), perhaps care should be exercised in placing quantitative significance on their data. The possibility of the effect of changing solvent species participation as a function of structure or of the buttressing effect of the meta substituent also was not considered.