JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY
(Registered in U. S. Patent Office) (Copyright, 1954, by the American Chemical Society)
VOLUME 76 JANUARY 21, 1954 NUMBER 1

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Aromatic Electrophilic Substitution by Hydrogen. III. The Mechanism of the Acid-catalyzed Decarboxylation of Aromatic Aldehydes[1,2]

BY W. M. SCHUBERT AND ROLAND E. ZAHLER

RECEIVED JULY 20, 1953

The rates of decarbonylation of 2,4,6-trimethyl-, 2,4,6-triethyl- and 2,4,6-triisopropylbenzaldehydes were determined in sulfuric acid ranging from 50 to 100% strength, and in the presence of added salts. The pK_a^B values of the three aldehydes were determined. Although the Hammett equation is followed in the case of mesitaldehyde over a limited range of sulfuric acid percentage, the rate data taken as a whole show the reaction does not occur by the Hammett unimolecular mechanism. The possibility of this being true of other reactions that follow the Hammett equation is discussed. The decarbonylation also does not occur by specific oxonium or molecular sulfuric acid catalysis. The rate-controlling step appears to be a bimolecular proton transfer, although termolecular processes cannot be ruled out. Rate, activation energy and activation entropy data are interpreted in terms of the proposed reaction mechanisms and the structure of the aldehydes.

Introduction

It has been found that 2,4,6-trialkylbenzaldehydes, when heated with strong acids, give carbon monoxide in nearly quantitative yield. The symmetrical trialkylbenzene is the other product except under conditions that lead to sulfonation of the hydrocarbon. The over-all reaction is apparently electrophilic replacement of the formyl group by hydrogen. It appeared of interest to undertake a quantitative study of this reaction because of its analogy to acid-catalyzed aromatic decarboxylation[3] and deacylation.[4] Furthermore, such a study might contribute to an understanding of electrophilic aromatic substitution and of acid catalysis in strong acid media.

The acid-catalyzed decarbonylation was discovered by Bistrzycki and co-workers[5] who found that certain aromatic aldehydes, particularly those with *o*- or *p*- hydroxyl, methoxyl or methyl groups, gave varying yields of carbon monoxide when heated with concentrated sulfuric acid. The organic products of the reaction were not characterized or identified.

Electrophilic replacement of formyl by groups other than hydrogen is well known. For instance, bromination of salicylaldehyde gives 2,4,6-tribromophenol and carbon monoxide.[6] Also, many examples of replacement of aromatic formyl by a nitro group are reported.[7]

Experimental

Materials.—The 2,4,6-trialkylbenzaldehydes were prepared from the corresponding 1,3,5-trialkylbenzenes by the method of Fuson and co-workers[8] and fractionated through a 23 in. twisted wire gauze column. The aldehydes had the following properties: mesitaldehyde, b.p. 120–122° (15 mm.), n^{25}_D 1.5503, m.p. 8–9°; 2,4,6-triethylbenzaldehyde, b.p. 132–133° (9–10 mm.), n^{25}_D 1.5322; 2,4,6-triisopropylbenzaldehyde, b.p. 128–129.5° (5 mm.), n^{25}_D 1.5138.

Sulfuric acid and methanesulfonic acid solutions were made up as previously.[3] Sodium sulfate, C.P., was dried at 110°; C.P. ammonium sulfate and sodium dihydrogen phosphate were dried in a vacuum desiccator over potassium hydroxide pellets.

Kinetic Method.—Two methods for determining the rate of reaction were used, a gasometric and a spectrophotometric method. In the gasometric method the rate of carbon monoxide evolution was determined in the apparatus previously used for carbon dioxide evolution.[3] Because of the extreme insolubility of carbon monoxide it was unnecessary to presaturate the system with the gas. In most of the gasometric runs 0.2 to 0.3 g. of the trialkylbenzaldehyde was dissolved in 10 ml. of the mineral acid to give a solution about 0.1 molar in aldehyde. In a few runs in which some of the evolved gas was acidic (carbon dioxide, sulfur dioxide) an ascarite bulb was inserted in the apparatus near the surface of the reacting solution. The final buret reading, used as V_∞ in calculating the rate constant, was usually evaluated by adding 1% to the observed volume at 99% reaction ($t_{99\%} = 6.67 \times t_{50\%}$). The slowness of most runs made inadvisable the continuance past 99% reaction because of uncertainties in the final reading, particularly when gradual oxidation

---

(1) Presented in summary at the 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953.

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

(3) W. M. Schubert, THIS JOURNAL, **71**, 2639 (1949).

(4) W. M. Schubert and H. K. Latourette, *ibid.*, **74**, 1829 (1952).

(5) A. Bistrzycki and M. Fellmann, *Ber.*, **43**, 772 (1910); A. Bistrzycki and L. Ryncki, *Chem. Ztg.*, **36**, 403 (1912).

(6) A. W. Francis and A. J. Hill, THIS JOURNAL, **46**, 2498 (1924).

(7) See for example A. H. Solevay, *J. Chem. Soc.*, **95**, 1155 (1909); M. P. de Lange, *Rec. trav. chim.*, **45**, 19 (1926); J. van Alphen, *ibid.*, **46**, 195 (1927).

(8) R. C. Fuson, E. C. Horning, S. P. Rowland and M. L. Ward, *Org. Syntheses*, **23**, 57 (1943); R. C. Fuson, E. C. Horning, M. L. Ward, S. P. Rowland and J. L. Marsh, THIS JOURNAL, **64**, 31 (1952).

of the product accompanied the decarbonylation. Rate constants, k_{obsd}, were calculated from the slope of the best straight line obtained in a plot of log ($V_\infty - V$) *vs.* time. Points obtained during the period in which solution of the sample and thermal equilibrium were being attained (one to three minutes after mixing) and beyond 95% reaction were not included in the plot. In general such a plot was slightly concave upward in decarbonylations of mesitaldehyde and 2,4,6-triethylbenzaldehyde and convex upward with 2,4,6-triisopropylbenzaldehyde. A typical plot is shown in Fig. 1.

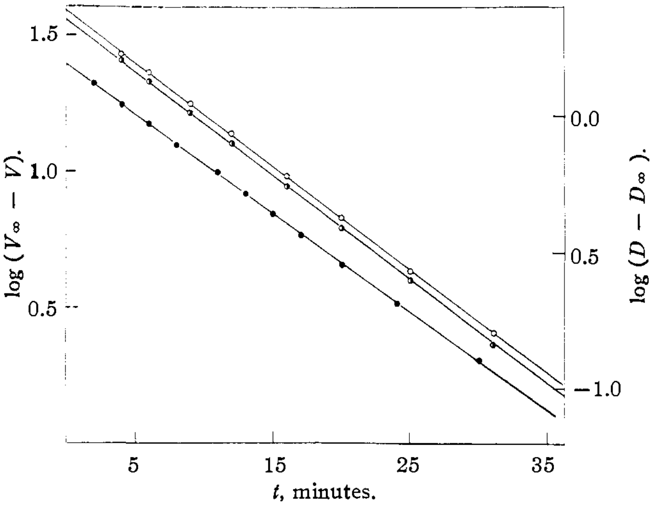


Fig. 1.—First-order plot, decarbonylation of mesitaldehyde at 100.0°: ○, spectrophotometric (10^{-5} molar in aldehyde) at 320 mμ, k_{obsd} = 1.46×10^{-3} sec.$^{-1}$; ◑, spectrophotometric (10^{-5} *M* in aldehyde) at 310 mμ, k_{obsd} = 1.46×10^{-3} sec.$^{-1}$; ●, gasometric (0.1 *M* in aldehyde), k_{obsd} = 1.40×10^{-3} sec.$^{-1}$.

In the spectrophotometric method, the rate of decline of the ultraviolet spectrum of the aldehyde was determined. In runs made at 100° and 90° a volume of the mineral acid solution (3×10^{-5} molar in aldehyde) was maintained at constant temperature and samples were withdrawn periodically. These samples were cooled quickly and the absorption spectrum determined at room temperature in a Beckman DU instrument at several wave lengths in the range of wave lengths 290 to 340 mμ. Runs at 80° and lower temperature were made by the method previously used for following rate of decarboxylation of 2,4,6-trihydroxybenzoic acid[9]; the reaction was actually run in quartz stoppered Beckman cells in a constant temperature bath that had been inserted between the photocell and monochrometer compartments of the Beckman DU instrument. The slope of the best straight line through a plot of log($D - D_\infty$) *vs.* time was used to obtain k_{obsd} for at least two wave lengths. Figure 1 shows a typical first-order plot for both the spectrophotometric and gasometric methods.

Products of Decarbonylation.—The gas resulting from the reaction of mesitaldehyde with 85% sulfuric acid was shown to be carbon monoxide by absorption in cuprous sulfate β-naphthol solution. In the kinetic runs reported below the normal yields of gas from the trimethyl, triethyl and triisopropylbenzaldehydes were, respectively, 99, 97 and 94%. Not over 3–4% of this gas, and generally much less, was absorbed by potassium hydroxide except in greater than 100% sulfuric acid.

An insoluble hydrocarbon layer was produced in the lower concentrations of sulfuric acid. The highest concentration in which its formation could be observed was 85%, 90% and 93% H_2SO_4 for the trimethyl, triethyl and triisopropyl aldehydes, respectively. In larger-scale runs, about 5 g. of aldehyde was warmed with 50 ml. of 83% sulfuric acid; the resulting hydrocarbon layer was separated, washed and distilled. Mesitaldehyde gave an 89% yield of mesitylene, b.p. 162–164°, $n^{25}D$ 1.4970, dinitro derivative, m.p. 85–86.5°; 2,4,6-triethylbenzaldehyde gave an 81% yield of 1,3,5-triethylbenzene, b.p. 210–215°, $n^{25}D$ 1.4938, trinitro derivative, m.p. 111–112°; 2,4,6-triisopropylbenzaldehyde gave a 78% yield of 1,3,5-triisopropylbenzene, b.p. 230–235°, $n^{25}D$ 1.4868, nitro derivative, m.p. 73–73.5°.

In the gasometric runs in more concentrated solutions of sulfuric acid, no hydrocarbon separated from the reaction mixture; presumably, trialkylbenzenesulfonic acids were produced. Considerable charring took place when the decarbonylation was slow relative to oxidation of products, as in 96 to 100% sulfuric acid and in methanesulfonic acid. No charring was discernible in the spectrophotometric runs, and the final spectrum remained constant, or at worst, increased only very slowly.

The Sulfonation of Mesitaldehyde.—Mesitaldehyde (1.9 g.) in 10 ml. of 102.9% sulfuric acid was shaken for three hours at 60°. During this period only 50 ml., 16% yield, of carbon monoxide was collected. The solution then was added with rapid stirring to 150 g. of ice-water, filtered through a sintered glass funnel, and the filtrate neutralized with solid sodium carbonate. After several hours, the precipitate was collected by suction filtration, dry weight 2.15 g. The material was recrystallized from water and dried in a vacuum desiccator over phosphorus pentoxide. The yield of white powder, presumably sodium 2,4,6-trimethyl-3-formylbenzenesulfonate, was 0.80 g.

Anal. Calcd. for $C_{10}H_{11}O_4SNa$: C, 47.99; H, 4.43; Na, 9.19. Found: C, 47.79; H, 4.45; Na, 9.20 (microanalyses by M. E. Taylor).

The pK_a of the 2,4,6-Trialkylbenzaldehydes.—The method of Hammett, Flexser and Dingwall[10] was used. The spectrum of each aldehyde was measured at room temperature in the range 230 to 350 mμ in various concentrations of sulfuric acid. Equation 1 was solved by the least squares method at a particular wave length in several strengths of acid for which ϵ_B and h_0 were known. The wave lengths chosen were in the region in which the ϵ_B reference curve was relatively flat. The pertinent spectral data and the calculated values of pK_a are given in Tables I, II and III.

$$K_a + \epsilon_{BH^+}\left(\frac{h_0}{\epsilon_B - \epsilon}\right) - \left(\frac{h_0\epsilon}{\epsilon_B - \epsilon}\right) = 0 \qquad (1)$$

Kinetic Results

The first-order rate constants obtained for the 2,4,6-trialkylbenzaldehydes, by both the gasometric and spectrophotometric methods are listed in Tables IV, V and VI. Unless otherwise stated the yields of gas in the gasometric runs was normal, *i.e.*, greater than 96% for mesitaldehyde and triethylbenzaldehyde, and greater than 94% for triisopropylbenzaldehyde.

Comparison of the rate constants obtained by the two methods reveal that they check each other well in the higher regions of sulfuric acid. The agreement is not so good in the lower percentage acid concentrations, where the gasometric method gives a noticeably lower value for k_{obsd}. This is believed due to the extraction of some of the reacting aldehyde by the hydrocarbon layer formed in the gasometric runs in lower acid concentration. In higher acid concentrations the gasometric reaction mixtures are homogeneous throughout the reaction (the sulfonic acid of the hydrocarbon is the product), and hence the agreement between the two methods is better. The spectrophotometric method proved on the whole to be a much more convenient method. Since it requires such a low concentration of substrate (10^{-5} *M*) it can be used in media in which the solubility of the substrate is limited. Also, effects of changing medium on individual substrate activity coefficients is at a minimum.

Decarbonylation and Desulfonation of Mesitaldehyde-3-Sulfonic Acid.—The reaction of mesitaldehyde-3-sulfonic acid with sulfuric acid, studied spectroscopically, gave the following results:

In 100.0% sulfuric acid, λ_{max} at 310 mμ, k_{obsd} at 100° = 0.08×10^{-3} sec.$^{-1}$. For mesitaldehyde, k_{obsd} = 0.63×10^{-3}.

In 90.3% sulfuric acid, λ_{max} = 308. The reaction at 100° shows an induction period, and is slower throughout than that of mesitaldehyde itself. This result was confirmed in a gasometric run.

---

[9] W. M. Schubert and J. D. Gardner, THIS JOURNAL, **75**, 1401 (1953).

[10] L. P. Hammett, C. A. Flexser and A. Dingwall, *ibid.*, **57**, 2103 (1935).

TABLE I

EXTINCTION COEFFICIENTS ($\epsilon \times 10^{-3}$) AND pK_a VALUES FOR MESITALDEHYDE IN $H_2SO_4 + H_2O$ MIXTURES

λ, mμ	% H_2SO_4 46.2[a]	51.2	55.9	60.4	65.6	70.2	75.1	80.4	$-pK_a$
305	4.11	5.58	8.06	11.78	16.90	19.10	20.50	20.80	4.37 ± 0.02
310	3.60	4.90	7.29	11.28	17.39	21.10	23.25	25.45	4.61 ± .06
315	3.00	4.05	6.14	9.74	16.04	20.30	24.60	27.75	4.65 ± .09
320	2.37	3.11	4.58	7.32	12.48	16.62	21.25	25.40	4.88 ± .11
325	1.77	2.26	3.22	4.88	7.99	10.85	14.65	18.50	4.49 ± .10
330	1.26	1.64	2.24	3.09	4.54	5.85	7.77	9.75	4.81 ± .20
335	0.92	1.20	1.64	2.20	2.88	3.28	3.89	4.42	4.32 ± .11
								Average	4.6

[a] Taken as spectrum of the free base.

TABLE II

EXTINCTION COEFFICIENTS ($\epsilon \times 10^{-3}$) AND pK_a VALUES FOR 2,4,6-TRIETHYLBENZALDEHYDE IN $H_2SO_4 + H_2O$ MIXTURES

λ, mμ	% H_2SO_4 50.6[a]	61.0	65.4	70.3	74.8	80.4	$-pK_a$
305	4.57	10.81	14.96	17.73	18.41	17.40	4.49 ± 0.07
310	4.06	10.71	15.97	20.45	22.32	22.30	4.71 ± .02
315	3.41	9.83	15.63	21.27	24.53	25.95	4.84 ± .02
320	2.74	8.09	13.56	19.48	23.95	26.35	4.99 ± .09
325	2.04	5.91	10.00	14.90	19.19	22.45	5.07 ± .11
330	1.48	3.94	6.44	9.31	12.35	14.87	5.09 ± .15
335	1.08	2.64	3.98	5.22	6.84	7.82	5.06 ± .10
						Average	4.9

[a] Taken as spectrum of free base.

TABLE III

EXTINCTION COEFFICIENTS ($\epsilon \times 10^{-3}$) AND pK_a VALUES FOR 2,4,6-TRIISOPROPYLBENZALDEHYDE IN $H_2SO_4 + H_2O$ MIXTURES

λ, mμ	EtOH[a]	% H_2SO_4 65.4	70.2	74.8	80.0	$-pK_a$
305	1.55	9.46	13.45	14.40	13.66	4.73 ± 0.08
310	1.18	10.20	15.93	18.18	18.13	4.93 ± .08
315	0.85	10.30	17.30	19.88	22.00	5.00 ± .14
320	0.47	9.33	16.73	21.78	23.50	5.14 ± .06
325	0.36	7.08	13.59	18.36	21.90	5.26 ± .04
330	0.18	5.18	9.74	13.53	16.50	5.30 ± .05
335	0.14	3.38	5.92	8.26	10.07	5.32 ± .11
340	0.09	2.33	3.66	4.66	5.56	5.08 ± .07
					Average	5.1

[a] Taken as spectrum of free base since aldehyde was insoluble in 60% H_2SO_4.

In 70.2% sulfuric acid the reaction also shows an induction period and is slower throughout than the mesitaldehyde decarbonylation. Originally λ_{max} was at 275 mμ (presumably the peak of the free base of mesitaldehyde-3-sulfonic acid), but as the reaction progressed a new absorption peak at 310 mμ (conjugate acid of mesitaldehyde) supplanted the original peak.

These conclusions may reasonably be drawn: (1) Mesitaldehyde-3-sulfonic acid decarbonylates one-eighth as fast as mesitaldehyde in 100% sulfuric acid, (2) mesitaldehyde-3-sulfonic acid desulfonates in sulfuric acid of 90% strength and below, forming mesitaldehyde which then decarbonylates, and (3) mesitaldehyde-3-sulfonic acid is a much weaker base than mesitaldehyde.

Decarbonylation of Formic Acid.—To determine if formic acid is a possible intermediate in the decarbonylation of the trialkylbenzaldehydes, its decarbonylation by the gasometric method under the same conditions was studied. The following rate constants were obtained at 100°: in 70.0% H_2SO_4, $k = 0.34 \times 10^{-3}$; in 75.0% H_2SO_4, $k = 1.5 \times 10^{-3}$. Since carbon monoxide is evolved faster from mesitaldehyde than from formic acid in 70% sulfuric acid, formic acid cannot have been an intermediate in the mesitaldehyde decarbonylation in that strength acid and presumably in other media. Some of the spectrophotometric rate constants in the 2,4,6-triisopropyl decarbonylation in lower acid percentages are much greater than for carbon monoxide evolution from for-

TABLE IV

FIRST-ORDER RATE CONSTANTS FOR THE DECARBONYLATION OF MESITALDEHYDE

1. In H_2SO_4 at 100.0°

Spectrophotometric % H_2SO_4	$10^3k_{obsd.}$ (sec.$^{-1}$)	Gasometric % H_2SO_4	$10^3k_{obsd.}$ (sec.$^{-1}$)
51.1	0.035	70.0	0.47, 0.47
60.3	.21	72.7	.71, .70
70.6	.75	75.0	.92, .94
74.6	1.21	77.7	1.12, 1.07
79.7	1.32	80.1	1.23, 1.27
85.2	1.46	82.9	1.34, 1.30
96.0	1.46	84.9	1.37, 1.38
98.1	1.14	87.6	1.43, 1.45
100.1	0.63	90.1	1.44, 1.52
		93.6	1.56, 1.57
		96.0	1.43, 1.40
		98.3	1.06, 1.04
		100.1	0.64, 0.62[a]
		100.4	0.6,[a,b] 0.8[c]
		100.8	1.3,[d] 1.3[d]

2. At various temperatures, spectrophotometric (85.2% H_2SO_4) and gasometric (84.9% H_2SO_4) methods

Temp., °C.	$10^3k_{obsd.}$ (sec.$^{-1}$) Spect.	Gas.
70.0	0.0498	....
80.0	.166	0.147
90.0	.518	0.456, 0.467
100.0	1.46	1.37, 1.38

3. In 100.1% H_2SO_4 at 100.0° with added substances, gasometric and spectrophotometric methods

Added substance	Molarity	$10^3k_{obsd.}$ (sec.$^{-1}$) Gas.	Spect.
$(NH_4)_2SO_4$	1.41	1.25[e]	..
$(NH_4)_2SO_4$	0.28	0.80	..
$(NH_4)_2SO_4$	0.84	1.10	..
$(NH_4)_2SO_4$	1.41	1.37	1.49
$(NH_4)_2SO_4$	2.34	1.40	..
$(NH_4)_2SO_4$	2.82	1.38	..
$(NH_4)_2SO_4$	3.00	..	1.60
Na_2SO_4	1.34	1.39	..
Na_2SO_4	1.41	1.36	..
NaH_2PO_4	1.41	1.37	..
$C_6H_5NO_2$	2.8	0.50	..
$C_6H_5NO_2$	5 ml./1 ml. H_2SO_4	0.30	..

4. In methanesulfonic acid at 100.0°, gasometric method

% CH_3SO_3H	$10^3k_{obsd.}$
92.0	0.30
99.7	.45

[a] With KOH trap in gas-collecting system. [b] Corrected for yield of carbon monoxide of 65%, assuming first-order competing reaction. [c] Corrected for yield of gas of 63%. [d] Corrected for yield of carbon monoxide of 25%. [e] Original concentration of H_2SO_4 was 86.4%.

TABLE V

FIRST-ORDER RATE CONSTANTS FOR THE DECARBONYLATION OF 2,4,6-TRIETHYLBENZALDEHYDE, GASOMETRIC METHOD

1. In H_2SO_4 at 100.0°

% H_2SO_4	$10^3k_{obsd.}$ (sec. $^{-1}$)
75.0	1.40,[a] 1.25[a]
77.5	2.87, 2.89
80.1	3.90, 3.79
82.5	4.53, 4.36
84.9	4.71, 4.75
87.5	4.72, 4.73
90.1	4.5,[b] 4.6[b]
93.0	3.4[b]
96.0	2.7[b]
100.1	1.1[b]

2. At various temperatures, spectrophotometric (85.2% H_2SO_4) and gasometric (84.9% H_2SO_4) methods

Temp., °C.	$10^3k_{obsd.}$ (sec. $^{-1}$) Spect.	Gas.
60.0	0.0785	....
70.0	.274	....
80.0	.743	0.601, 0.614
90.0	2.18	1.77, 1.76
100.0	...	4.71, 4.73

3. In methanesulfonic acid at 80.0°

% CH_3SO_3H	$10^3k_{obsd.}$ (sec. $^{-1}$)
99.7	0.33[c]

[a] Aldehyde not soluble at room temperature. [b] Rate constant not as reliable because of slow oxidation of the products. [c] Corrected for yield of gas of 80%, assuming first-order side reaction.

mic acid, but these constants do not measure carbon monoxide evolution directly. However, since the values of k_{obsd} obtained by the spectrophotometric and gasometric methods correspond in the regions where both methods can be used, it can be assumed the spectrophotometric k_{obsd} is a direct measure of rate of carbon monoxide evolution in the more dilute acids as well.

Discussion

In Fig. 2 are plotted the changes with percentage sulfuric acid of the pseudo-first order rate constant for decarbonylation, k_{obsd}, for each of the aldehydes studied: mesitaldehyde, 2,4,6-triethylbenzaldehyde and 2,4,6-triisopropylbenzaldehyde. The decline in k_{obsd} in the higher sulfuric acid concentrations occurs in regions of acid strength in which each aldehyde is practically completely in the form of its conjugate acid. This was ascertained by a determination of the pK_a values. The principal features of the rate *vs.* percentage sulfuric acid curves are (1) the appearance of a maximum for each aldehyde, (2) the maxima appear at a different percentage sulfuric acid for each aldehyde, and (3) the lower the percentage acid that the maximum in rate occurs, the greater is the ratio of maximum rate to rate in 100% sulfuric acid.

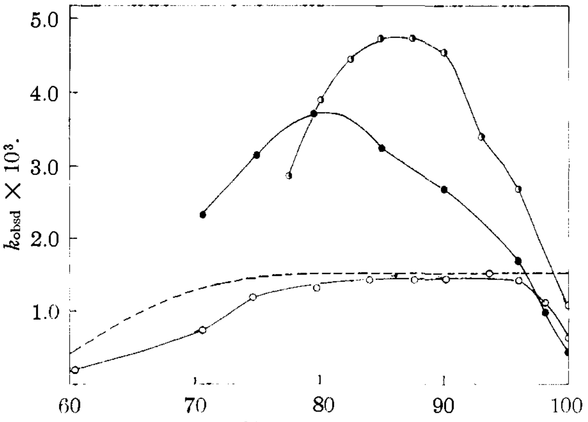


Fig. 2.—Change in k_{obsd} with % H_2SO_4: ○, mesitaldehyde at 100.0°: ◑, 2,4,6-triethylbenzaldehyde at 100.0°; ●, 2,4,6-triisopropylbenzaldehyde at 80.0°; ---, theoretical unimolecular k_{obsd} calculated from equation 4.

TABLE VI

FIRST-ORDER RATE CONSTANTS FOR THE DECARBONYLATION OF 2,4,6-TRIISOPROPYLBENZALDEHYDE

1. In H_2SO_4 at 80.0°

Spectrophotometric		Gasometric	
% H_2SO_4	$10^3k_{obsd.}$ (sec. $^{-1}$)	% H_2SO_4	$10^3k_{obsd.}$ (sec. $^{-1}$)
70.6	2.33	82.5	2.1[a]
74.9	3.16	84.9	2.6, 2.6
79.9	3.71	90.1	2.5
84.9	3.24	93.0	2.0
90.3	2.70	96.0	1.3, 1.3
96.0	1.71	100.1	0.49, 0.50
98.1	1.01		
100.1	0.43		

2. Effect of initial concentration of aldehyde on gasometric rate constant in 84.9% H_2SO_4 at 80.0°

Concn., *M*	$10^3k_{obsd.}$ (sec. $^{-1}$)
0.06	2.9
.12	2.6
.28	2.1
.15[b]	1.7

3. At various temperatures, spectrophotometric (85.2% H_2SO_4) and gasometric (84.9% H_2SO_4) methods

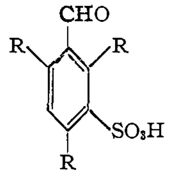
Temp., °C.	$10^3k_{obsd.}$ (sec. $^{-1}$) Spect.	Gas.
50.0	0.149	....
60.0	0.476	....
70.0	1.33	1.07, 1.08
80.0	3.43	2.80, 2.93
90.0	...	7.30, 7.52

4. Effect of added salts in 100.1% H_2SO_4 at 80.0°, spectrophotometric method

Added substance	Molarity	$10^3k_{obsd.}$ (sec. $^{-1}$)
Na_2SO_4	1.40	1.66
$(NH_4)_2SO_4$	1.40	1.76
$(NH_4)_2SO_4$	3.10	3.75

[a] Aldehyde not soluble at room temperature. [b] Five ml. of 1,3,5-triisopropylbenzene added initially.

The observed decline in k_{obsd} near 100% sulfuric acid cannot be attributed to any side equilibrium lowering the concentration of the reactive species. In the first place there is no evidence of a second ionization (beyond conjugate acid formation) of the aldehydes. Thus the spectrum of each aldehyde remains constant (100% ionization to BH^+) except for a small medium shift in 80 to 100% sulfuric acid. Secondly, a possible side reaction forming the aldehyde–sulfonic acid I cannot account for the decline in k_{obsd}. There is no evidence in the zero time spectra for formation of I which is a weaker base than the unsulfonated aldehyde and would change the spectrum of the sulfuric acid solutions. Furthermore, the sulfonic acid of mesitaldehyde (I, R = CH_3) was prepared in 103% sulfuric acid and its behavior (see Kinetic Results) shows it cannot have been formed from mesitaldehyde in 100% or lower percentage sulfuric acid. The sulfonic acids of 2,4,6-triethyl- and 2,4,6-triisopropylbenzaldehydes should be formed even less readily, if the carbonyl or protonated carbonyl group exerts any appreciable deactivating effect (no very large inhibition of resonance is evident in the spectrum of the aldehydes), since the corresponding hydrocarbons begin to be sulfonated in 90 and 93% sulfuric acid whereas mesitylene begins to be sulfonated in about 85% sulfuric acid.



I

Various added salts, all essentially sources of bisulfate ion, had a marked accelerating effect on the mesitaldehyde decarbonylation in 100% sulfuric acid. In 1.4 *M* solution, ammonium sulfate, sodium sulfate, sodium dihydrogen phosphate and "oxonium sulfate" all showed about the same accelerating effect. A somewhat larger accelerating effect was shown by water than by ammonium sulfate in higher concentrations of added salt (see Fig. 3).

Several possible reaction paths will now be considered in light of the effect of changing media and changing structure of the aldehyde on the rate.

The Unimolecular Mechanism.—As a convenient starting point the agreement of the mesitaldehyde decarbonylation data with the Hammett unimolecular mechanism 2 was examined

$$B + HA_i \rightleftarrows BH^{\oplus} + A_i \quad \text{fast} \qquad (1)$$

$$BH^{\oplus} \xrightarrow{k_2} \text{Prods.} \quad \text{slow} \qquad (2)$$

From the Brönsted rate equation 3, the kinetic equations 4, 5 and 6 are easily derived.[4,11]

$$v = k_{\text{obsd}}([B] + [BH^{\oplus}]) = k_2[BH^{\oplus}]f_{BH^{\oplus}}/f_{tr^{\oplus}} \qquad (3)$$

$$k_{\text{obsd}} = k_2 \frac{[BH^{\oplus}]}{[B] + [BH^{\oplus}]}\frac{f_{BH^{\oplus}}}{f_{tr^{\oplus}}} = k_2' \frac{[BH^{\oplus}]}{[B] + [BH^{\oplus}]} \qquad (4)$$

$$\log k + H_0 - \log \frac{[B]}{[B] + [BH^{\oplus}]} = \text{const., assume} \quad \frac{f_{BH^{\oplus}}}{f_{tr^{\oplus}}} = \text{const.} \qquad (5)$$

$$\log k + H_0 = \text{constant, } [BH^{\oplus}] << [B] \qquad (6)$$

In media in which the concentration of $BH^{\oplus}$ is large relative to B, equation 3 is a more convenient test of the unimolecular mechanism than the equation in H_0, equation 5. It is immediately apparent that unless the activity coefficient ratio $f_{BH^{\oplus}}/f_{tr^{\oplus}}$ suffers an unexpectedly large change there should be no decline in k_{obsd} in the higher acid concentrations. For the mesitaldehyde decarbonylation, assuming as usual that $f_{BH^{\oplus}}/f_{tr^{\oplus}}$ is constant, the unimolecular mechanism predicts that k_{obsd} should follow the dotted line of Fig. 2 (if k'_2 is taken to have the maximum value of actual k_{obsd}). Values of the ratio $[BH^{\oplus}]/([B] + [BH^{\oplus}])$ used to calculate points on the dotted line were obtained from the value −4.6 for the pK_a of mesitaldehyde, determined at room temperature.[12]

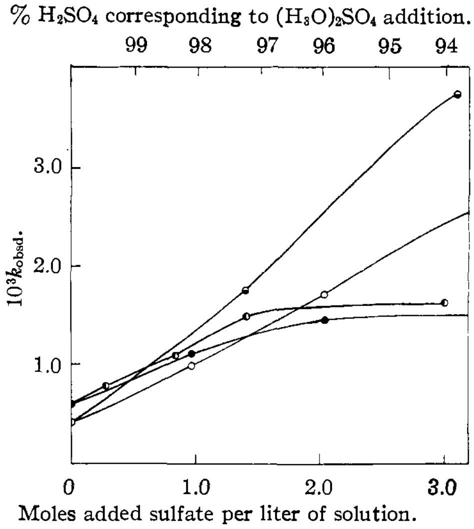


Fig. 3.—Effect of adding H_2O [calculated as $(H_3O)_2SO_4$] or $(NH_4)_2SO_4$ on the rate of decarbonylation in 100% H_2SO_4: ●, mesitaldehyde + $(H_3O)_2SO_4$ at 100.0°; ◐, mesitaldehyde + $(NH_4)_2SO_4$ at 100.0°; ○, 2,4,6-triisopropylbenzaldehyde + $(H_3O)_2SO_4$ at 80°; ◒, 2,4,6-triisopropylbenzaldehyde + $(NH_4)_2SO_4$ at 80°.

A comparison of the dotted line with the observed for mesitaldehyde in Fig. 2 shows that from about 75 to 95% sulfuric acid the agreement with the unimolecular mechanism is quite good. In fact the agreement over this arbitrary range is as good as has been found for many reactions to which the "unimolecular" mechanism has been assigned because of the relative constancy of the logarithmic sum of equation 6 or 5.[4,11] Most of these previous studies were made over relatively narrow ranges of acid percentage, and in all but one instance[4] the concentration of $BH^{\oplus}$ was negligible relative to B.

The apparent deviations from unimolecular behavior of the mesitaldehyde decarbonylation in lower percentage sulfuric acid solutions could be due to the use of the wrong pK_a value. For example, a pK_a value of −5.1 instead of −4.6 would bring the theoretical, dotted line of Fig. 2 into close coincidence with the observed curve in the region of 60 to 95% sulfuric acid. However, the deviations from unimolecular behavior in greater than 95% sulfuric acid cannot be explained on the basis of an error in pK_a, nor is there any evidence of a side equilibrium lowering the concentration of the reactive species of the aldehyde. Therefore, for the unimolecular mechanism to prevail the activity coefficient ratio $f_{BH^{\oplus}}/f_{tr^{\oplus}}$ would have to change more than twofold in from 95% to 100% sulfuric acid *while remaining relatively constant in 75% to 95% sulfuric acid.* Such a large change in $f_{BH^{\oplus}}/f_{tr^{\oplus}}$ does not seem likely since the transition state

---

(11) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 273–275.

(12) The degree of ionization of mesitaldehyde does not appear to be changed substantially with temperature. In 61.0 and 70.2% sulfuric acid, the spectrum at 60° was found to be practically the same as at room temperature.

in the unimolecular mechanism would be not only of the same charge type as $BH^{\oplus}$, but would be the same species, in an activated state of perhaps somewhat different configuration. Furthermore, the substrate concentration is very low (10^{-5} *M*).

The deviation from apparent unimolecular behavior of 2,4,6-triethyl- and 2,4,6-triisopropylbenzaldehyde is even larger. For the unimolecular mechanism to prevail in the case of 2,4,6-triethylbenzaldehyde would require a fourfold decrease in $f_{BH^{\oplus}}/f_{tr^{\oplus}}$ in 87 to 100% sulfuric acid; in the case of 2,4,6-triisopropylbenzaldehyde the value of this activity coefficient ratio in 100% sulfuric acid would have to be 10% of its value in 80% sulfuric acid.

The deviations of the decarbonylation reaction from unimolecular behavior suggest strongly the participation of solvent species that are declining in concentration or catalytic effectiveness near 100% sulfuric acid. Accordingly, various bi- and termolecular mechanisms were considered.

Bimolecular Mechanisms.—Two bimolecular paths, 8 and 9, are considered. In these HA_i is any solvent acid ($H_3O^{\oplus}$, H_2SO_4 and $H_3SO_4^{\oplus}$ to a limited extent near 100% sulfuric acid) and A_i is any solvent base (H_2O, $HSO_4^{\ominus}$, H_2SO_4).

$$B + HA_i \rightleftarrows BH^{\oplus} + A_i;\ K_{a_i} = \frac{a_B a_{HA_i}}{a_{BH^{\oplus}} a_{A_i}} \quad (7)$$

$$BH^{\oplus} + A_i \xrightarrow{k_i} \text{Prods.};\ v = \sum_i k_i a_{BH^{\oplus}} a_{A_i}/f_{tr_i} \quad (8)$$

or

$$B + HA_i \xrightarrow{k_i'} \text{Prods.};\ v = \sum_i k_i' a_B a_{HA_i}/f_{tr_i} \quad (9)$$

The Brönsted equation for 8 or 9 leads to the equivalent rate expressions 10 or 11.[13]

$$k_{obsd} = \frac{v}{[B] + [BH^{\oplus}]} = \frac{1}{[B]+[BH^{\oplus}]} \sum_i k_i a_{BH^{\oplus}} a_{A_i}/f_{tr_i} \quad (10)$$

$$k_{obsd} = \frac{1}{[B] + [BH^{\oplus}]} \sum_i k' K_{a_i} a_{BH^{\oplus}} a_{A_i}/f_{tr_i} \quad (11)$$

$$k_{obsd} = \frac{[BH^{\oplus}]}{[B] + [BH^{\oplus}]}[k_{H_2O} a_{H_2O} f_{BH^{\oplus}}/f_{tr^{\oplus}} + k_{HSO_4^{\ominus}} a_{HSO_4^{\ominus}} f_{BH^{\oplus}}/f_{tr} + k_{H_2SO_4} a_{H_2SO_4} f_{BH^{\oplus}}/f_{tr^{\oplus}}] \quad (12)$$

The rate expression 12 appears to agree qualitatively with the experimental facts. If attention is confined to regions of acid strength (*i.e.*, greater than about 75% sulfuric acid) in which the ratio $[BH^{\oplus}]/([B] + [BH^{\oplus}])$ is practically unity, then variations in k_{obsd} should follow variations of the quantity in brackets. The approximate variations with percentage sulfuric acid of each of the activity terms of equation 12 are plotted in Fig. 4. Presumably the only activity coefficient ratio, $f_{BH^{\oplus}}/f_{tr_i}$, subject to possible large variation with changing acid concentration is the one in the second term in which the transition state has net zero charge. If either of the bimolecular mechanisms is assumed to prevail, the following points emerge from an examination of the rate data in light of the quantity in brackets of equation 12: (1) The rate-controlling step cannot be one of specific acid or base catalysis (*i.e.*, HA_i being *only* H_2SO_4, or $H_3O^{\oplus}$ or $H_3SO_4^{\oplus}$; or A_i being only $HSO_4^{\ominus}$, or H_2O or H_2SO_4). If specific acid or base catalysis prevailed the shape of the curves of Fig. 2 should be the same for each aldehyde in the region of practically complete ionization to $BH^{\oplus}$ (*i.e.*, in greater than about 75% sulfuric acid). At least two of the three terms of equation 12 are apparently playing a role in the decarbonylations to account for the absence of more than one rate maximum and the smoothness of the k_{obsd} *vs.* percentage sulfuric acid plots. (2) The appreciable rates in 100% sulfuric acid are accountable mainly to the third term. (3) In the mesitaldehyde decarbonylation, a proper balance of the three terms leading to an approximate constancy of the sum in 75 to 95% sulfuric acid and a decline in the sum in 95 to 100% sulfuric acid to somewhat less than half is not inconceivable. (4) A decrease in the relative value of $k_{H_2SO_4}$ to $k_{HSO_4^{\ominus}}$ (perhaps accompanied by an increase in the relative value of k_{H_2O}) can account for the rate maximum being at successively lower percentages in progressing from trimethyl- to triethyl- to triisopropylbenzaldehyde. (5) Decreasing relative value of $k_{H_2SO_4}$ also is reflected in the increase in the ratio of maximum rate to rate in 100% sulfuric acid in progressing from trimethyl- to triisopropylbenzaldehyde. (6) The accelerating effect of various salts, all sources of bisulfate ion when added to 100% sulfuric acid, is accommodated by the second term in brackets. The accelerating effect is less for trimethyl- than for triisopropylbenzaldehyde. In agreement with points 4 and 5 above, this would mean the ratio $k_{H_2SO_4}/k_{HSO_4^{\ominus}}$ is least for triisopropylbenzaldehyde, the first term in brackets being negligible in 100% sulfuric acid. The fact that water in low percentages has a smaller accelerating effect than ammonium sulfate (Fig. 3) suggests that water may be a less potent source of bisulfate ion (*i.e.*, incompletely ionized to $H_3O^{\oplus}$ and $HSO_4^{\ominus}$) and that k_{H_2O} is smaller than $k_{HSO_4^{\ominus}}$.

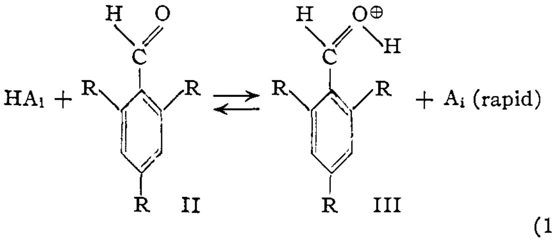
On the basis of the evidence thus far, either reaction path 8 or 9 appears plausible; termolecular mechanisms also cannot be ruled out. For 9 to be the rate-controlling step it would have to take the course depicted by equation 14 rather than the forward process of equation 13 since a proton transfer to the carbonyl oxygen to give the conjugate acid III is very rapid. If 14 represents the rate-controlling process this would presumably be followed by a faster step, such as 15, giving the final products. A concerted cyclic mechanism[3] such as 16 is not considered likely in the highly polar medium for the reaction.

For the rate-controlling step to be 8 it would presumably take the course depicted by equation 15. If 15 is the rate-controlling step, it would have to be preceded by a more rapid and possibly reversible step, 14. Running the reaction with ArCOD should distinguish between 14 or 15 as the rate-controlling step. Attack of A_i on the carbonyl

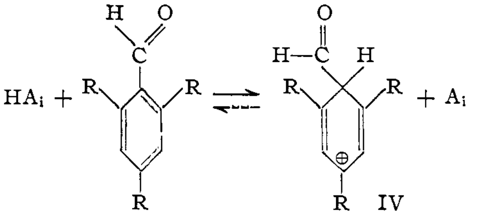
---

(13) An equivalent rate expression is obtained regardless of whether the $BH^{\oplus}$ taking place in the rate-controlling step is the oxonium salt of the aldehyde or a different conjugate acid $BH^{\oplus\prime}$ (*e.g.*, compound IV) formed in small amount in an accompanying equilibrium. It is easily shown from the equilibrium constants for $BH^{\oplus}$ and $BH^{\oplus\prime}$, that $a_{BH^{\oplus\prime}} = a_{BH^{\oplus}} K_{a_i}/K'_{a_i}$. Also, $v = k_{obsd.}([B] + [BH^{\oplus}] + [BH^{\oplus\prime}]) \approx k_{obsd.}([B] + [BH^{\oplus}])$.

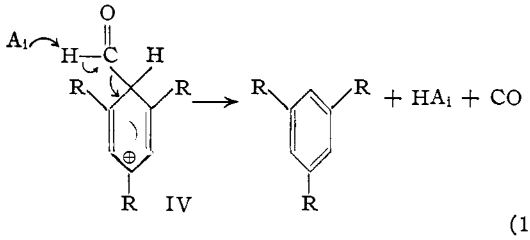
carbon is ruled out since formic acid is not an intermediate.



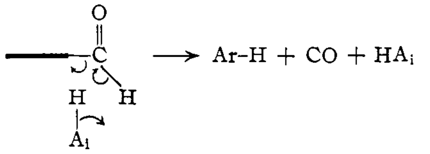
(13)



(14)



(15)



(16)

Termolecular Mechanisms.—Three possible termolecular reaction paths need be considered. These are shown in equations 17, 18 and 19. Of

$$B + HA_i + A_j \xrightarrow{k_{ij}} \text{Products} \quad (17)$$

$$BH^+ + A_i + A_j \longrightarrow \text{Products} \quad (18)$$

$$BH^+ + A_j + HA_i \xrightarrow{k_{ij}} \text{Products} \quad (19)$$

these three processes, 18 can be rejected on the grounds there is no reasonable electronic mechanism to fit it.

For the Lowry-type mechanism 17, the Brönsted rate equation leads to 20. The same rate expression can be derived for mechanism 18. The terms under the summation sign do not appear

$$k_{\text{obsd}} = \frac{[\text{BH}^{\oplus}]}{[\text{B}] + [\text{BH}^{\oplus}]} \sum_{\text{ij}} k_{\text{ij}} K_{\text{ai}} a_{\text{Ai}} a_{\text{Aj}} \frac{f_{\text{BH}^{\oplus}}}{f_{tr\text{li}}};\ K_{\text{ai}} = \frac{a_{\text{HAi}} a_{\text{B}}}{a_{\text{Ai}} a_{\text{BH}^{\oplus}}} \quad (20)$$

to lend themselves to ready simplification. At best one can say that it is not inconceivable that the rather flexible quantity under the summation sign can change, with changing media and structure of aldehyde, in conformity with the experimental results.

The rate equation 21 for the reaction path 19 can be expanded more profitably. Altogether there are nine activity product terms under the summation sign (since there are to be considered three acids, $H_3O^{\oplus}$, H_2SO_4 and $H_3SO_4^{\oplus}$ and three bases, H_2O, $HSO_4^{\ominus}$ and H_2SO_4). If some of these terms are reasonably neglected and those that are related by an equilibrium constant are combined, equation 22 results.

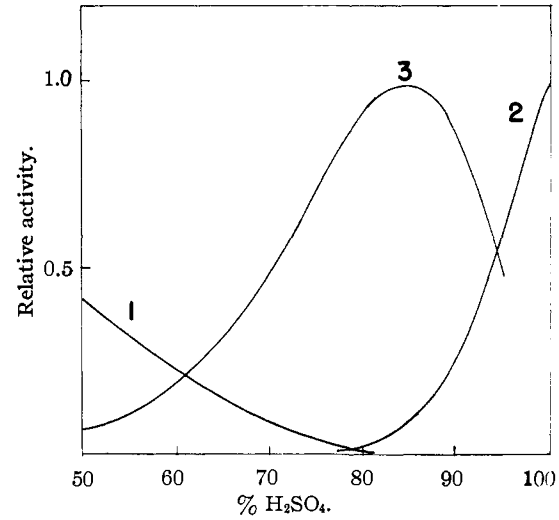


Fig. 4.—Plot of activity *vs.* % H_2SO_4: 1, a_{H_2O}, calculated from vapor pressure data[14]; 2, $a_{H_2SO_4}$, calculated values of Abel[15]; 3, $a_{HSO_4^-}$, estimated assuming maximum (height of maximum arbitrary) in sulfuric acid monohydrate.

$$k_{\text{obsd}} = \frac{[\text{BH}^{\oplus}]}{[\text{B}] + [\text{BH}^{\oplus})} \sum_{\text{ij}} k'_{\text{ij}} a_{\text{HAi}} a_{\text{Ai}} \frac{f_{\text{BH}^{\oplus}}}{f_{\text{trij}}} \quad (21)$$

$$k_{\text{obsd}} = \frac{[\text{BH}^{\oplus}]}{[\text{B}] + [\text{BH}^{\oplus}]} \left[k_{\text{I}} a_{\text{H}_3\text{O}^{\oplus}} a_{\text{H}_2\text{O}} \frac{f_{\text{BH}^{\oplus}}}{f_{\text{tr}^{++}}} + k_{\text{II}} a_{\text{H}_3\text{O}^{\oplus}} a_{\text{HSO}_4^{\ominus}} \frac{f_{\text{BH}^{\oplus}}}{f_{\text{tr}^{\oplus}}} + k_{\text{III}} a_{\text{H}_2\text{SO}_4} a_{\text{HSO}_4^{\ominus}} \frac{f_{\text{BH}^{\oplus}}}{f_{\text{tr}}} + k_{\text{IV}} a_{\text{H}_2\text{SO}_4} a_{\text{H}_2\text{SO}_4} \frac{f_{\text{BH}^{\oplus}}}{f_{\text{tr}^{\oplus}}} \right] \quad (22)$$

Confining attention to media in which the ratio $[\text{BH}^{\oplus}]/([\text{B}] + [\text{BH}^{\oplus}])$ is unity, the bracketed quantity of equation 22 can be imagined to vary in the necessary manner. The four terms should have maxima in the following percentages of sulfuric acid: term I, maximum below 85%; term II, maximum in about 85% (monohydrate); term III, maximum between 85 and 100%, say approximately 90%; term IV, maximum in 100% sulfuric acid. A proper balance of these four terms could account for the apparent unimolecularity of the mesitaldehyde decarbonylation in 75 to 95% sulfuric acid and the gradual decline in rate in 95 to 100% acid. The appearance of rate maxima in lower percentage sulfuric acid for 2,4,6-triethyl- and 2,4,6-triisopropylbenzaldehyde can be attributed to relatively greater oxonium and bisulfate ion catalysis (*i.e.*, higher relative values of k_{I} and k_{II}). Greater oxonium and bisulfate ion catalysis for triisopropylbenzaldehyde would also be reflected in the greater ratio of maximum rate to rate in 100% sulfuric acid. Finally, the bisulfate ion catalysis demonstrated by the addition of various salts would be accommodated by terms II and III.

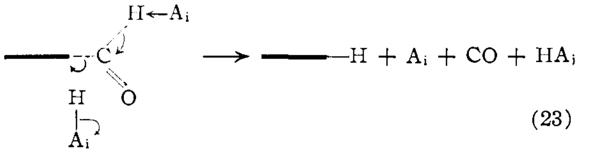
Reaction 17 would presumably occur *via* mechanism 23, and reaction 19 *via* mechanism 24, 25 or 26. Mechanisms 23 and 25 should show an iso-

---

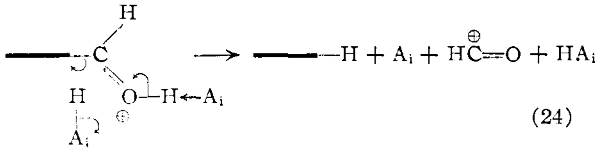
(14) "International Critical Tables," Vol. III, p. 303.

(15) E. Abel, *J. Phys. Chem.*, **50**, 260 (1946); **52**, 908 (1948).

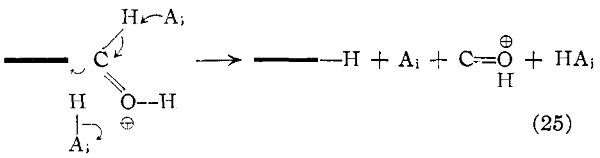
tope effect with ArCOD, whereas 24 and 26 should not.



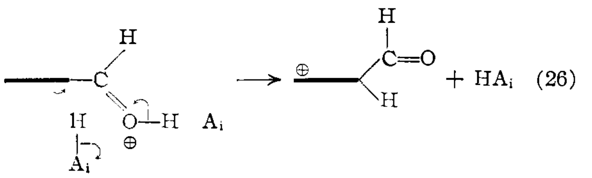
(23)



(24)



(25)



(26)

Possible Generality of Non-unimolecular Mechanisms.—It is considered not unlikely that other reactions in strong acid media, which show apparent unimolecular behavior (*i.e.*, for which the sum of equation 8 was found relatively constant), may indeed proceed by bimolecular or termolecular mechanisms. Possible polymolecular behavior of these reactions may not have been detected because (1) they were studied usually over rather narrow ranges of mineral acid percentages, and (2) they were studied in media in which $[BH^{\oplus}] << [B]$. Thus changes in acid percentage produced large changes in the relative concentrations of $BH^{\oplus}$, thereby possibly covering up any effects of participation of solvent species in the rate-controlling step.

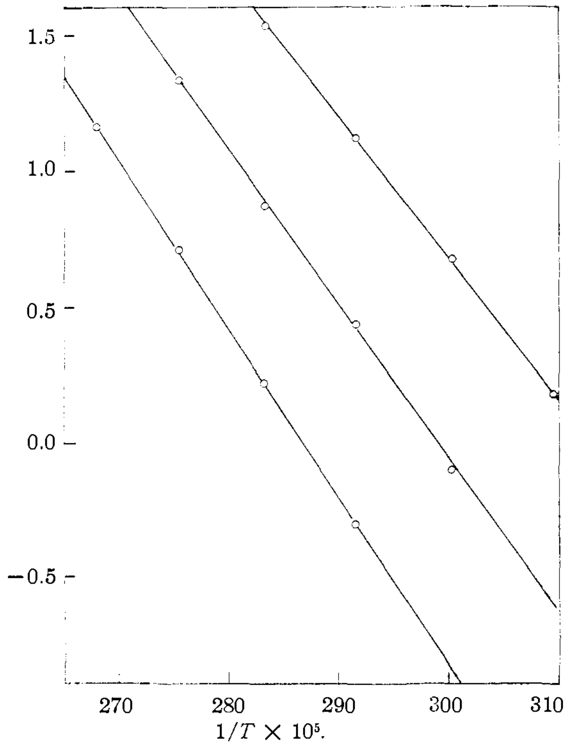


Fig. 5.—Activation energy plot: top line, 2,4,6-triisopropylbenzaldehyde; middle line, 2,4,6-triethylbenzaldehyde; bottom line, mesitaldehyde.

The Effect of Aldehyde Structure.—Considering firstly the effect of structure on the value of pK_a for the aldehydes, the decreasing basicity of II as R is changed from methyl to ethyl to isopropyl probably is due at least in part to decreased stabilization of III (as compared to II) by hyperconjugation. Another possible factor is increased steric interference with the charge distribution in III as the bulk of R is increased. Steric inhibition of resonance is reflected in the somewhat lower ϵ of the conjugate acid of triisopropylbenzaldehyde at the peak at 320 mμ.

Activation energies, activation entropies and comparative rates of reaction for the three aldehydes are listed in Table VII. These were measured by both the gasometric and spectrophotometric methods in a concentration of sulfuric acid in which the rates are at or near a maximum. The experimental activation energy in 84% sulfuric acid by the spectrophotometric method was obtained from Fig. 5. The "gasometric" activation energy in 84.9% sulfuric acid was obtained from a similar plot at only three temperatures. For reasons discussed in the Experimental section, the values of Table VII obtained by the spectrophotometric method are considered more reliable, although the two methods check each other well. The differences in the values of Table VII are large enough to be of significance and can be interpreted in terms of the ground and transition states of the reacting aldehydes. The activation energy differences favor an increase in rate in going from trimethyl- to triisopropylbenzaldehyde, and the entropies of activation operate in the opposite direction.

TABLE VII

Spectrophotometric values 85.2% H_2SO_4	2,4,6-Trialkylbenzaldehyde Methyl	Ethyl	Isopropyl
Relative k (80.0°)	1	4.5	20.6
E_A, kcal.	28.6	26.1	24.3
$\Delta S^\ddagger$, e.u.[a]	2.8	−1.3	−3.4
Gasometric values, 84.9% H_2SO_4			
Relative k (80.0°)	1	4.1	19.5
E_A, kcal.	29.1	26.9	23.8
$\Delta S^\ddagger$, e.u.	3.9	0.7	−5.1

[a] Calculated for 80° using equation:[16] $k = \frac{ekT}{h} e^{\Delta S^\ddagger/R} e^{-E_A/RT}$.

Care must be exercised in interpreting the data of Table VII, since k_{obsd} is a complex function containing various k_i as expressed by equation 12, 19 or 20. Fortunately the quantity $[BH^{\oplus}]/([B] + [BH^{\oplus}])$ can be assumed constant (*i.e.*, unity) with changing temperature in 85% sulfuric acid. The

---

(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

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_i or k_{ij} 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.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

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

RECEIVED JULY 20, 1953

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).