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Aromatic Electrophilic Substitution by Hydrogen. III. The Acid-Catalysed
Decarbonylation of 2,4,6-Trialkylbenzaldehydes.

By W. M. Schubert and Roland E. Zahler

The rate of decarbonylation of mesitaldehyde was determined by a gasometric method in 70 to 102.9% sulfuric acid at 100°. The kinetics in 70 to 96% sulfuric acid is fairly consistent with the rate-controlling step being a unimolecular rearrangement of the conjugate acid; but the decline in rate in 96 to 100% sulfuric acid and the effect of added salts is explainable only in terms of reactions of higher molecularity involving one or more solvent species. The possibility of other acid-catalyzed reactions which appear to be unimolecular in the slow step actually being polymolecular is discussed. The comparative rates of decarbonylation under comparable conditions of mesitaldehyde, 2,4,6-triethylbenzaldehyde, and 2,4,6-triisopropylbenzaldehyde are 14.1:17.7. One or more steric factors are apparently being exerted.

Introduction

Certain aromatic aldehydes, particularly those with ortho or para hydroxyl, methoxyl, or methyl groups, were shown by Bistrzycki and coworkers to give varying yields of carbon monoxide when treated with hot concentrated sulfuric acid.¹ The

- (1) A. Bistrzycki and H. Fellmann, Ber., 43, 772 (1910); A. Bistrzycki and L. Rynicki, Chem. Ztg., 36, 403 (1912).

organic products of the reaction were not characterized or identified. There are also numerous instances in which an aromatic formyl group is replaced by an electrophilic reagent other than hydrogen to yield carbon monoxide as a gaseous product. For example, bromination of salicylaldehyde gives 2,4,6-tribromophenol and carbon monoxide.² Many examples are known in which a formyl group has been replaced by a

- (2) A. W. Francis and A. J. Hill, This Journal, 46, 2498 (1924).

nitro group.³

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

In these laboratories 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 give sulfonation of the hydrocarbon. The overall reaction appeared to be electrophilic replacement of the formyl group by hydrogen (equation 1). It would thus be an example



of the aromatic elimination reaction and formally analogous to aromatic decarboxyla-

tion⁴ and decomposition.⁵ A kinetic study of the reaction was undertaken, since the

(4) W. M. Schubert, This Journal, 71, 2639 (1949).

(5) W. M. Schubert and H. K. Latourrette, ibid., 74, 1829 (1952).

evolution of carbon monoxide provided a convenient means of following the reaction.

Experimental

Materials - The 2,4,6-trialkylbenzaldehydes were prepared from the corresponding 1,3,5-trialkylbenzenes by the method of Fuson and coworkers⁶ and fractionated through

(6) 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 (1942).

a 23 in. twisted wire gauze column. The aldehydes had the following properties: mesitaldehyde, b.p. 120-122° (15 mm.), n_D^{25} 1.5503, m.p. 8-9°; 2,4,6-triethylbenzaldehyde, b.p. 132-133° (9-10 mm.), n_D^{25} 1.5322; 2,4,6-triisopropylbenzaldehyde, b.p. 128-129.5° (5 mm.), n_D^{25} 1.5138.

Sulfuric acid and methanesulfonic acid solutions were made up as previously.⁵ Phosphorus pentoxide, C. P., was mixed with C. P. 85% phosphoric acid to obtain 97% phosphoric acid. 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 - For most of the runs the rate of reaction was followed by determining the rate of carbon monoxide evolution by the gasometric method and in the apparatus previously used for carbon dioxide evolution.⁴ In these runs 0.2 to 0.3 g. of aldehyde was dissolved in 10 ml. of the mineral acid solution, to give about a 0.1 molar solution. In a few of the runs in which some of the evolved gas

was acidic an ascarite bulb was placed near the surface of the solution in the gas collecting apparatus.

A few of the rate constants were determined spectroscopically. A solution about 3×10^{-5} molar in aldehyde was heated at constant temperature. Samples were withdrawn periodically, cooled quickly, and the ultraviolet absorption spectra determined at room temperature in the range of wave lengths from 250 to 350 mμ.

First order rate constants were obtained from the slope of the best straight line through the points in a plot of time vs. $\log (V_{\infty} - V)$, where V is volume of carbon monoxide, or a plot of time vs. $\log (D_{\infty} - D)$, where D is optical density. Points 2-3 min. after the start of the reaction (time for solution of sample and temperature equilibrium) and past 95% reaction were not considered. Since many of the runs were slow and others complicated by very slow oxidation of the product, V_{∞} was calculated by adding 1% to V at the time of 99% reaction ($t_{99\%} = 6.67 \times t_{50\%}$). In Fig. 1 is shown a first order plot of a typical run. In general such a plot was slightly concave upwards in decarboxylations of mesitaldehyde and 2,4,6-triethylbenzaldehyde and convex upwards with 2,4,6-triisopropylbenzaldehyde.

Products of Decarboxylation - 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 was absorbed by potassium hydroxide until it was attempted to run the reaction in sulfuric acid above 100% concentration.

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 acid; the resulting hydrocarbon layer was separated, washed and distilled.

Mesitylaldehyde gave an 89% yield of mesitylene, b.p. 162-164°, n_D^{25} 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_D^{25} 1.4930, trinitroderivative, m.p. 111-112°; 2,4,6-trisopropylbenzaldehyde gave a 70% yield of 1,3,5-trisopropylbenzene, b. p. 230-235°, n_D^{25} 1.4860, nitroderivative, m.p. 73-73.5°.

In the more concentrated solutions of sulfuric acid, no hydrocarbon separated from the reaction mixture; presumably, trialkylbenzenesulfonic acids were produced. Considerable charring took place when the decarboxylation was slow relative to oxidation of products, as in 96 to 100% sulfuric acid and in methanesulfonic acid.

The Sulfonation of Mesitylaldehyde - Mesitylaldehyde (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 Mesitylaldehyde - The pK_a of mesitylaldehyde was determined spectrally in the ultra-violet at room temperature by the method of Hammett, Fleischer, and Dingwall.⁷

(7) L. P. Hammett, L. A. Fleischer, and A. Dingwall, ibid., 57, 2103 (1935).

The spectrum in the range 230 to 350 m μ in various concentrations of sulfuric acid

was measured (see Fig. 2). Two methods were used to calculate the pK_a . The first of these involved least squares solution of equation (2) in two unknowns, K_a and ϵ_{BH} . Equation (2) was solved at a particular wave length in several strengths of acid for which values of ϵ_B and h_0 were known. The wave lengths chosen were in the region in which the ϵ_B curve (the reference curve in 46.2% sulfuric acid) was relatively flat, and hence the medium effect of a lateral shift in spectrum small.⁷

The pertinent spectral data and the calculated values of pK_a are given in Table I.

$$K_a + \epsilon_{BH} + \left(\frac{h_0}{\epsilon_B - \epsilon} \right) - \left(\frac{h_0}{\epsilon_B' - \epsilon} \right) = 0 \quad (2)$$

Table I

Values of extinction coefficient ($\epsilon \times 10^{-3}$) for
Benzaldehyde in H_2SO_4 - water mixtures at room temp.

λ (m μ)	$\% \text{H}_2\text{SO}_4$												Soln. of 4-25 (NH ₄) ₂ SO ₄ in	
	3.2	40.2	51.2	55.9	60.4	65.6	70.2	75.2	80.4	84.8	90.3	100.0	100.0	1-1/250
340	.13	.62	.85	1.30	1.79	2.26	2.42	2.62	2.56	2.55	2.75	2.44	3.10	
330	.47	1.26	1.64	2.24	3.09	4.54	5.85	7.77	9.75	10.87	12.60	13.17	12.14	
320	1.24	2.37	3.11	4.58	7.32	12.46	16.62	21.25	25.4	26.6	29.05	29.4	27.7	
310	2.15	3.60	4.90	7.29	11.28	17.39	21.1	23.25	25.45	24.75	25.8	25.25	25.4	
300	2.58	4.73	6.24	8.59	11.69	15.18	15.87	15.97	15.22	13.83	13.87	13.07	14.23	
290	3.92	7.63	9.03	10.44	11.51	11.27	9.49	7.92	6.36	5.50	5.28	4.84	5.56	
280	9.33	12.65	13.02	12.73	11.39	8.25	5.35	3.54	2.11	1.79	1.66	1.57	1.77	
270	14.02	13.37	12.51	11.00	8.68	5.20	2.83	1.57	.51	.61	.42	.52	.53	
260	11.50	9.96	7.42	6.37	4.71	2.56	1.31	.81	.21	.36	.31	.26	.37	
250	6.05	4.31	3.16	2.90	2.24	1.34	.81	.71	.70	.56	.57	.44	.69	

The isobestic point method⁷ was also used to determine pK_a . The curves of Fig. 2 were arbitrarily shifted to intersect at 290 mμ. Equation (3) was then solved at several wave lengths for each concentration of sulfuric acid. The calculations are summarized in Table II.

$$pK_a = H_0 - \log \frac{[B]}{[BH^+]} = H_0 - \log \frac{\epsilon - \epsilon_{BH^+}}{\epsilon_B - \epsilon} \quad (3)$$

Table II

-pK_a Values for Mesitaldehyde Computed by the Least Squares Method of Flexner, Hammett and Dingwall

		% H ₂ SO ₄							
mμ	Eq.	51.2	55.9	60.4	65.6	70.2	75.1	Ave.	Dev.
340	2	4.26	4.17	4.22	4.34	4.65	4.17	4.30	.13
330	2	4.59	4.65	4.78	4.99	5.22	4.64	4.82	.20
320	2	4.78	4.78	4.83	4.95	5.14	4.79	4.88	.11
310	2	4.53	4.53	4.57	4.64	4.75	4.62	4.61	.06
300	2	4.18	4.17	4.16	3.90	3.84	4.16	4.07	.13
280	3	5.13	5.22	5.07	5.06	5.17	5.34	5.17	.08
270	2	4.48	4.49	4.56	4.65	4.72	4.53	4.57	.08
260	3	4.81	4.55	4.54	4.63	4.80	5.11	4.74	.17
250	3	4.44	4.55	4.49	4.47	4.19	3.75	4.32	.23
Average								4.61	.26

Table III

$-pK_a$ Values for Mesitaldehyde Computed
by the Isobestic Point Method

	% H_2SO_4						Ave.	Dev.
mp	51.2	55.9	60.4	65.6	70.2	75.1		
320	4.46	4.49	4.56	4.61	4.81		4.59	.10
310	4.60	4.63	4.72	4.87	5.16	5.35	4.89	.25
300	4.57	4.58	4.67	4.85	5.17	5.38	4.87	.27
290	isobestic point							
280	4.73	4.73	4.77	4.84	4.92	5.13	4.85	.11
270		4.88	4.84	4.88	5.02	5.23	4.97	.10
260			4.93	4.95	5.09	5.33	5.08	.16
Ave.	4.59	4.66	4.75	4.83	5.03	5.28	4.88	.11

Average of all values: $4.87 \pm .20$

Atting 75% H_2SO_4 : 4.79

The upward drift of $-pK_a$ with increasing % H_2SO_4 can be related to the medium effect on ϵ_{BH} . If the reference curve for spectrum of BH were displaced to correct for this, it would tend to diminish the amount of drift, at least between 300-320 mp.

The Approximate Basicities of 2,4,6-Triethylbenzaldehyde and 2,4,6-Trisopropylbenzaldehyde - The pK_a values for these two aldehydes was not accurately determined, but their spectra^a at room temperature in a few concentrations of sulfuric acid ^{were} determined (Figs. 3 and 4). It can be seen by an inspection of the spectra that 2,4,6-triethylbenzaldehyde and 2,4,6-trisopropylbenzaldehyde are of about the same base strength as mesitaldehyde (see Fig. 2) and that they are apparently completely ionized to BH^+ in 80 % sulfuric acid.

Kinetic Results

Decarbonylation of Mesitaldehyde - Most of the kinetic runs were made on mesitaldehyde. The effect of different acids, added salts, temperature, and concentration of aldehyde were studied. The results are summarized in Table IV.

Table IV

Decarbonylation of Mesitaldehyde

A. Effect of Aldehyde Concentration in 84.9% H_2SO_4 at 100.0°

Conc. of aldehyde, moles/liter	$10^3 k$ (sec. ⁻¹)
0.06	1.40
0.13	1.37, 1.38
0.25	1.27

B. Effect of Temperature in 84.9% H_2SO_4

Temp., °C	$10^3 k$ (sec. ⁻¹)
80.0	0.347
90.0	0.456, 0.467
100.0	1.37, 1.38

Table IV (cont'd)

C. Effect of Concentration of H_2SO_4 at 100.0°

% H_2SO_4	$10^3 k$ (sec. ⁻¹)	Yield of gas, %
70.0	0.47, 0.47	99, 98
72.7	0.705, 0.702	100
75.0	0.917, 0.938	100, 99
77.7	1.12, 1.07	100, 100
80.1	1.23, 1.27	100, 98
82.9	1.34, 1.30	100, 101
84.9	1.37, 1.38	98, 100
87.6	1.43, 1.45	99, 99
90.1	1.56, 1.57	96, 98
93.6	1.56, 1.57	97, 97
96.0	1.43, 1.48	97, 97 ^a
98.3	1.01 ^b	97
100.1	0.64, 0.64	94, 90 ^a
100.4	0.8 or less ^c	63
100.8	1.3 ^{b,d}	37, 25 ^a
102.6	---	13
102.9	---	11

D. Effect of Added Salts in 100% H_2SO_4 at 100°

Salt	Molar Concentration	$10^3 k$ (sec. ⁻¹)	Yield of gas, %
$(\text{NH}_4)_2\text{SO}_4$	0.28	0.85	95
$(\text{NH}_4)_2\text{SO}_4$	0.84	1.16	96
$(\text{NH}_4)_2\text{SO}_4$	1.4	1.40	---
$(\text{NH}_4)_2\text{SO}_4$	2.8	1.40	97
$(\text{NH}_4)_2\text{SO}_4$	4.15	0.88	95
Na_2SO_4	1.41	1.42	97
NaH_2PO_4	1.41	1.37	---

2,4,6-Triethylbenzaldehyde - This compound reacted more rapidly than mesitaldehyde as shown in Table V. Gas evolution due to oxidation of triethylbenzene had to be taken into account at concentrations of sulfuric acid above 90%.

Table V

Decarbonylation of 2,4,6-triethylbenzaldehyde

A. Effect of Temperature in 84.9% H_2SO_4

Temp., °C	$10^3 k(sec^{-1})$
80.0	.601, .614
90.0	1.77, 1.76
100.0	4.71, 4.73

B. Effect of Sulfuric Acid Concentration at 100°C

% H_2SO_4	$10^3 k(sec^{-1})$	Yield of gas, %
77.5	2.87, 2.89	
80.1	3.90, 3.79	97
82.5	4.53, 4.36	
84.9	4.72, 4.73	97
87.5	4.72, 4.73	
90.1	4.5, 4.6 ^a	98
93.0	3.4 ^a	
96.0	2.7 ^a	101 (99) ^b
100.1	1.1 ^a	99 (96) ^b

^a Estimated after correcting for oxidation of triethylbenzene.

^b With an ascarite trap.

Decarbonylation of 2,4,6-triisopropylbenzaldehyde - This aldehyde was the most reactive, and most runs were made at 80°. The results are summarized in Table VI.

Table VI

Decarbonylation of 2,4,6-Triisopropylbenzaldehyde

A. Effect of concentration of H_2SO_4 at 80.0°

% H_2SO_4	$10^3 k(\text{sec.}^{-1})$	Yield of gas, %
84.9	2.6, 2.6, 1.7 ^a	94
87.5	2.7, 2.6	
90.1	2.5	94
93.0	1.8 ^b	85
96.0	1.0 ^b	66, 69 ^c
100.1	0.5	94, 90 ^c
100.1	1.41 ^d	--
100.8	0.3 ^b	96, 61 ^c

^a 5.5 ml. of 1,3,5-triisopropylbenzene added.

^b Corrected for yield of CO and oxidation of product.

^c Ascarite tube above reaction surface.

^d Na_2SO_4 added to a concentration of 1.4 molar.

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

In 100.0% sulfuric acid, $\lambda_{\text{max}} = 310$, k_{observed} at 100° = $0.08 \times 10^{-3} \text{ sec.}^{-1}$.

For mesitaldehyde, by the same method, $k_{\text{obs}} = 0.64 \times 10^{-3}$.

In 90.3% sulfuric acid, $\lambda_{\text{max}} = 308$. The reaction at 100°C. shows an induction period, and is slower throughout than that of mesitaldehyde itself. This result was confirmed in a gasometric run -- after 30% of the total gas had come off, the first order rate law was obeyed with $k_{\text{observed}} = 0.73 \times 10^{-3}$.

In 70.2% sulfuric acid, at 70°C., the spectral changes shown in Fig. 5 were

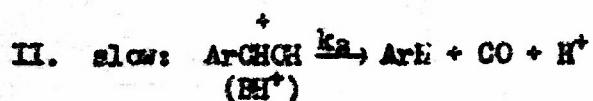
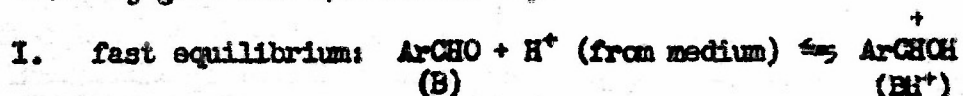
noted. Originally, $\lambda_{\text{max}} = 275 \text{ m}\mu$, but as the reaction progresses a new absorption peak at $310 \text{ m}\mu$ supplants it.

These conclusions may reasonably be drawn: (1) Mesitaldehyde 3-sulfonic acid decarbonylates one-eighth as fast as mesitaldehyde, (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.

Decarboxylation of Formic Acid - To determine if formic acid is a possible intermediate in the decarboxylation of the trialkylbenzaldehydes, its decarboxylation 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 , $k = 1.5 \times 10^{-3}$. Apparently, formic acid cannot have been an intermediate.

Discussion

Mechanism of Decarbonylation - In Fig. 6 ^{are} plotted the changes with percent sulfuric acid of the first order rate constants for the decarbonylation of mesitaldehyde, 2,4,6-triethylbenzaldehyde and 2,4,6-triisopropylbenzaldehyde. A maximum in rate is observed for each aldehyde although the shapes of the curves differ from one aldehyde to the next. Of the three aldehydes, mesitaldehyde could be studied over a wider range of sulfuric acid concentration because of its greater solubility. For it, the data up to the point at which the rate begins to drop off appreciably ^{are} ~~is~~ consistent with the rate controlling step being a unimolecular rearrangement of the conjugate acid (mechanism II).



Mechanism II was proposed for the acid-catalyzed decylation of aromatic ketones⁵ and had been tested by the constancy of the sum of equation (5) derived from the Brønsted rate equation (2).

$$\underline{v} = \underline{k}_2 [\text{BH}^+] \frac{f_{\text{BH}^+}}{f_{\text{tr}^+}} \quad (2)$$

$$\underline{k} = \frac{\underline{v}}{[\text{B}] + [\text{BH}^+]} = \underline{k}_2 \frac{[\text{BH}^+]}{[\text{B}] + [\text{BH}^+]} \frac{f_{\text{BH}^+}}{f_{\text{tr}^+}} \quad (3)$$

Also

$$\underline{k} = \underline{k}_3 K \frac{[\text{B}]}{[\text{B}] + [\text{BH}^+]} a_{\text{H}^+} + \frac{f_{\text{B}}}{f_{\text{tr}^+}}, \text{ where } K = \frac{f_{\text{BH}^+}}{a_{\text{H}^+} + a_{\text{B}}} \quad (4)$$

Hence

$$\log \underline{k} + 11.0 - \log \frac{[\text{B}]}{[\text{B}] + [\text{BH}^+]} = \text{const.}, \text{ assuming } \frac{f_{\text{B}} f_{\text{BH}^+}}{f_{\text{tr}^+} f_{\text{C}}} = \text{const.}^8 \quad (5)$$

(8) This sort of assumption was first made by Hammett, c.f. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc. New York, N. Y., 1940, Chapter IX.

Or, assuming $f_{\text{BH}^+}/f_{\text{tr}^+} = \text{const.}^5$

$$\underline{k}'_2 = \text{const.} \times \underline{k}_2 = \underline{k} \frac{[\text{B}] + [\text{BH}^+]}{[\text{BH}^+]} \quad (6)$$

And

$$\log \underline{k}'_2 = \log \underline{k} + \log \frac{[\text{B}] + [\text{BH}^+]}{[\text{BH}^+]} \quad (7)$$

Equations (6) or (7) are more convenient to use when $[\text{BH}^+]$ is large relative to $[\text{B}]$. This is the case with mesitaldehyde which is largely in the form of its conjugate acid in 80% sulfuric acid. In Table VII are tabulated the quantities $\underline{k}'_2$ and $\log \underline{k}'_2$ for the decarboxylation, values of the ratio $([\text{B} + \text{BH}^+])/[\text{BH}^+]$ being obtained from the measured $\text{p}K_{\text{a}}$ ($\text{p}K_{\text{a}} = -4.7$) and equation (3). For comparative purposes, values of $\underline{k}'_2$ and $\log \underline{k}'_2$ for the decylation of 2,6-dimethylacetophenone⁵ are included.

Table VII

Values of k'_2 and $\log k'_2$ for the Decarbonylation of Mesitaldehyde and the Deacylation of 2,6-Dimethylacetophenone.

H_2SO_4	Decarbonylation			Deacylation		
	$([\text{DH}]/[\text{D}]) \cdot ([\text{H}]/[\text{H}'])$	$10^3 k'_2$	$\log k'_2$	$[\text{DH}]/([\text{D} + \text{DH}'])$	$10^3 k'_2$	$\log k'_2$
70.0	.88	0.54	-3.27	---	---	---
72.7	.93	0.75	-3.12	.01	0.31	-3.51
75.0	.97	0.96	-3.02	.02	0.42	-3.38
77.7	.98	1.12	-2.95	.05	0.51	-3.29
80.1	.99	1.26	-2.90	.09	0.55	-3.26
82.9	1.00	1.32	-2.88	.19	0.56	-3.25
84.9	"	1.35	-2.87	.40	0.58	-3.24
87.6	"	1.44	-2.84	.57	0.66	-3.18
90.1	"	1.48	-2.83	.70	0.72	-3.14
93.6	"	1.54	-2.81	.83	0.74	-3.13
96.0	"	1.42	-2.85	.92	0.76	-3.12
98.3	"	1.02	-2.99	---	---	---
100.1	"	0.58	-3.24	---	---	---

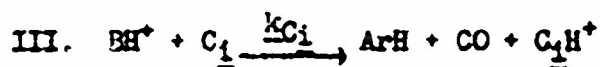
It can be seen that k'_2 for the decarbonylation of mesitaldehyde is reasonably constant in the region 76 to 96% sulfuric acid. Furthermore, k'_2 and $\log k'_2$ are as constant for the decarbonylation as for the deacylation. Indeed, $\log k'_2$ is a constant as is the corresponding logarithmic sum of equation (8) for many other reactions for which a unimolecular mechanism such as II has been assumed to prevail.^{8,9} Equation (8) is equivalent, of course, to the more general equation

9) L. P. Hammett and A. L. Deyrup, This Journal, 54, 2738 (1932).

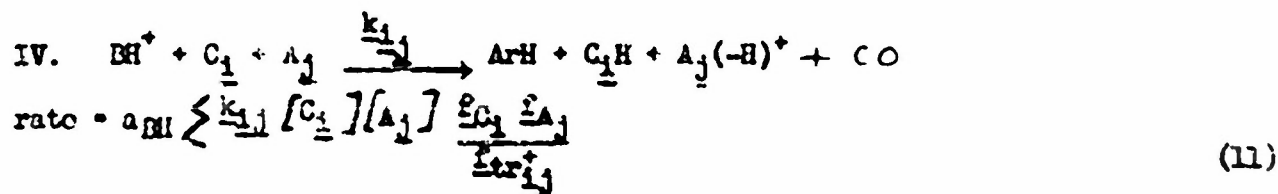
(7) in regions of negligible BH^+ concentration.

$$\log k + F_0 = \text{Const.} \quad (8)$$

Although the unimolecular mechanism II fits well for decarbonylation of mesitaldehyde in up to 96% sulfuric acid, it does not account for the decline in rate beyond that point. The deviation from constancy of k_2 in the higher percentage of sulfuric acid cannot be made attributable to an error in pK_a as could the deviation in 70% acid. Nor can the decline in rate be attributed to prior formation of mesitaldehydesulfonic acid followed by its slow decarbonylation (see Kinetic Results). Instead, it is suggested that the decline in rate, which occurs in lower percentages of acid and is more marked with 2,4,6-triethylbenzaldehyde and 2,4,6-trisopropylbenzaldehyde, is due to changes in the concentration of one or more solvent species which participate in the rate-controlling step. This step thus may be bimolecular such as III, or termolecular such as IV. C_1 represents any base (e.g. H_2O , HSO_4^- , H_2SO_4) and A_1 any acid (e.g. H_3O^+ , H_2SO_4 , $H_3SO_4^+$) effective in the reaction.



$$\text{rate} = a_{BH^+} \left\{ \frac{K_{C1}}{K_{tr1}} [C_1] \frac{f_{C1}}{f_{tr1}} - [BH^+] \left[k_{H_2O} [H_2O] \frac{f_{BH^+} f_{H_2O}}{f_{tr+}} + \cancel{k_{HSO_4^-}} \right. \right. \\ \left. \left. + k_{H_2SO_4} [H_2SO_4] \frac{f_{BH^+} f_{H_2SO_4}}{f_{tr+}} \right] \right\} \quad (10)$$



For mechanism III to prevail, the quantity $\frac{K_{C1}}{K_{tr1}} [C_1]$ of equation (10) must decline in higher percentages of sulfuric acid and remain relatively constant in

the lower percentages (neglecting activity coefficient terms). Mechanism III can account for the decline in rate in the higher percentages of sulfuric acid, provided $k_{H_2SO_4}$ is small because of the weakness of H_2SO_4 as a base, since $[H_2O]$ and $[HSO_4^-]$ are both declining. The differences in the shape of the curves of Fig. 6 for 2,4,6-triethylbenzaldehyde, 2,4,6-triisopropylbenzaldehyde and mesitaldehyde can also be accounted for since the relative values of k_{H_2O} , $k_{HSO_4^-}$, and $k_{H_2SO_4}$ would not be expected to be the same for the three aldehydes. In the lower percentages of sulfuric acid, $\sum k_{C_i} [C_i]$ would be constant provided $k_{HSO_4^-}$ is greater than k_{H_2O} (neglecting the term involving $k_{H_2SO_4}$) since $[H_2O]$ is probably increasing more rapidly than $[HSO_4^-]$ is decreasing in lowering percentages of sulfuric acid below mono-hydrate strength (84.5%).

For the "termolecular" mechanism IV to prevail, the quantity $\sum k_{A_j} [C_i] [A_j]$ must be relatively constant in lower acid concentrations and declining in the region between 85 and 100% acid. The number of terms in the summation is reduced if attention is confined to regions in which the solvent ionization occurs principally according to equation V, with little VI (i.e. below ca. 99.7% sulfuric acid). The number of terms can be reduced still further for regions in which terms involving H_2SO_4 functioning as a base are small. Equation (11) then reduces to (12), if the activity coefficient terms are neglected:

$$\text{rate} = [H^+] \left[\frac{k_{H_2O, H_3O^+}}{[H_2O, H_3O^+]} [H_2O] [H_3O^+] + \frac{k_{H_2O, H_2SO_4}}{[H_2O, H_2SO_4]} [H_2O] [H_2SO_4] + \frac{k_{HSO_4^-, H_3O^+}}{[HSO_4^-, H_3O^+]} [HSO_4^-] [H_3O^+] + \frac{k_{HSO_4^-, H_2SO_4}}{[HSO_4^-, H_2SO_4]} [HSO_4^-] [H_2SO_4] \right] \quad (12)$$

It is not unlikely that the quantity in brackets in equation (12) decreases with increasing sulfuric acid strength beyond 84.5% (mono-hydrate) since the separate terms would appear to be changing as follows: the first term decreasing, the second and third terms changing in the same direction (since $[H_2O] [H_2SO_4] = K [H_3O^+] [HSO_4^-]$) and decreasing; and the fourth term decreasing some. A proper balance of rate constants and

concentration terms could account for the relative constancy of k_1 up to the concentration of acid in which the rate begins to decline. In this region, the separate terms in brackets appear to be changing as follows with increasing acid strength: the first term decreasing, since $[H_2O]$ is decreasing more rapidly than $[H_3O^+]$ is increasing; the second and third terms increasing proportionately (with the second term probably small); the fourth, probably small though increasing.

Not only is the appearance of a maximum in the rate indicative of the participation of solvent species in the rate-controlling step. The effect of added salts (Table IV) also supports the view that a base participates as per a mechanism such as III or IV. The addition of bisulfate ion in the form of ammonium or sodium sulfate to 100% sulfuric acid enhances the rate, indicating that bisulfate ion participates in the reaction. In fact these salts have a greater effect up to 2 moles of added sulfate per liter than the equivalent amount of water in enhancing the rate. This may indicate incomplete ionization of the water¹⁰ to

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- (10) R. J. Gillespie, J. Chem. Soc., 2493 (1950) concluded from cryoscopic measurements that the ionization of water lacks 6% of being complete in 100% sulfuric acid.
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H_3O^+ and HSO_4^- and that bisulfate ion is a more effective base than water in the reaction.

The decreased effectiveness of ammonium sulfate in four molar concentration (Fig. 7) is worth noting. This cannot be attributed to any appreciable decrease in $ArCH_3^+$ concentration for the addition of the ammonium sulfate caused no appreciable change in the ultra-violet spectrum of the solution (see Table I). It may mean that the addition of that much salt has lowered the concentration of effective acid species for a reaction such as IV.

Possible Extent of Bi- or Termolecular Mechanisms in Acid-Catalysis - Other acid-catalyzed reactions heretofore considered to proceed by unimolecular reaction^{8,9} of the conjugate acid, BH^+ , may in actuality proceed by mechanisms such as III or IV. The participation of polymolecular mechanisms may not have been detected because of a balance in rate constants and concentrations of solvent species. Most of the reactions described have been studied over a narrow range of acid strength. Furthermore, the effect on the rate-controlling step of changing the medium may have been obscured in these cases by the large percentage change in $[BH^+]$ which occurs when $[BH^+]$ is small relative to $[B]$. Thus by way of contrast with mesitaldehyde decarbonylation, the addition of bases (water, sulfates, etc.) to 100% sulfuric acid retards acid catalyzed decomposition of malic acid;^{11,8}

(11) E. L. Whitford, This Journal, 47, 953 (1925).

here the added bases inhibit ionization to BH^+ , covering up the catalytic effect of basic species.

A detailed examination of the effect of changing medium on acid-catalyzed reactions in which ionization of the organic material to BH^+ is complete and observable over a wide range of acid concentration is being undertaken.

Comparative Rates of Decarbonylation - The comparative rates of decarbonylation in 84.9% sulfuric acid at 80° of mesitaldehyde, 2,4,6-triethylbenzaldehyde, and 2,4,6-triisopropylbenzaldehyde are 1:4.1:17.7. In 84.9% sulfuric acid each of the aldehydes is practically completely in the form of the conjugate acid (Figs. 2, 3 and 4). Furthermore the rate of decarbonylation in 84.9% sulfuric acid is at or near the maximum for each aldehyde. Therefore, they are being compared at as near comparable conditions as possible. The activation energy in

84.9% sulfuric acid is 29.1, 26.9 and 23.8 for mesitaldehyde, 2,4,6-triethylbenzaldehyde and 2,4,6-triisopropylbenzaldehyde (Fig. 8). The values of the A factor in 84.9% sulfuric acid for mesitaldehyde, 2,4,6-triethylbenzaldehyde, and 2,4,6-triisopropylbenzaldehyde are 1.5×10^{11} , 2.9×10^{13} , and 1.5×10^{12} ; the entropies of activation are 3.9, 0.7 and -5.1 e.u. respectively.¹²

(12) $\Delta S^\ddagger$ at 80° was calculated using the equation, $k_2 = \frac{e}{h} \frac{kT}{e} e^{-E_{\text{exp}}/RT} e^{\Delta S^\ddagger/R}$

Cf. S. Gladstone, K. J. Laidler, and H. Eyring "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1944, p. 199.

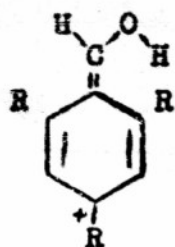
The rate and activation energy differences appear large enough to warrant conclusions as to the effect of the alkyl substituents on the reaction. The alkyl substituents no doubt exert an electron release effect to enhance the electrophilic displacement of the formyl group by a proton. This electron release effect in the transition state, presumably at least partly hyperconjugative, should be in the order isopropyl > ethyl > methyl which is, however, opposite to the effect of these groups on the decarboxylation rate. The operation of steric factors, such as suggested for the decarboxylation of mesitoic acid,⁴ is indicated.

Firstly, there may be a steric inhibition of resonance effect. Dipole moment studies by Kadesch and Waller¹³ indicate that resonance interaction of the

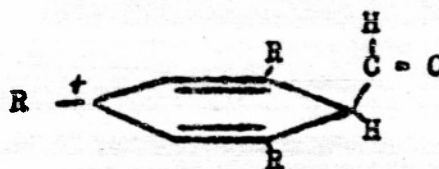
(13) R. G. Kadesch and S. W. Waller, This Journal, 63, 1310 (1944).

carbonyl group of mesitaldehyde with the ring is inhibited but little, if at all. However, more resonance inhibition may prevail in the conjugate acid and should be increased as the bulk of the ortho substituent is increased. Thus, the larger the ortho alkyl group, the smaller the contribution of structures such as I to the

state of the starting conjugate acid. The conjugate acid will then have a higher energy (the larger R is) relative to the tetrahedral transition state of which II is a sterically uninhibited contributing structure. Another steric function of the ortho substituents may be to help force the reacting molecule into a favored configuration for reaction (i.e. the non-coplanar configuration such as II).



I (inhibited)



II (uninhibited)

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Fig. 1

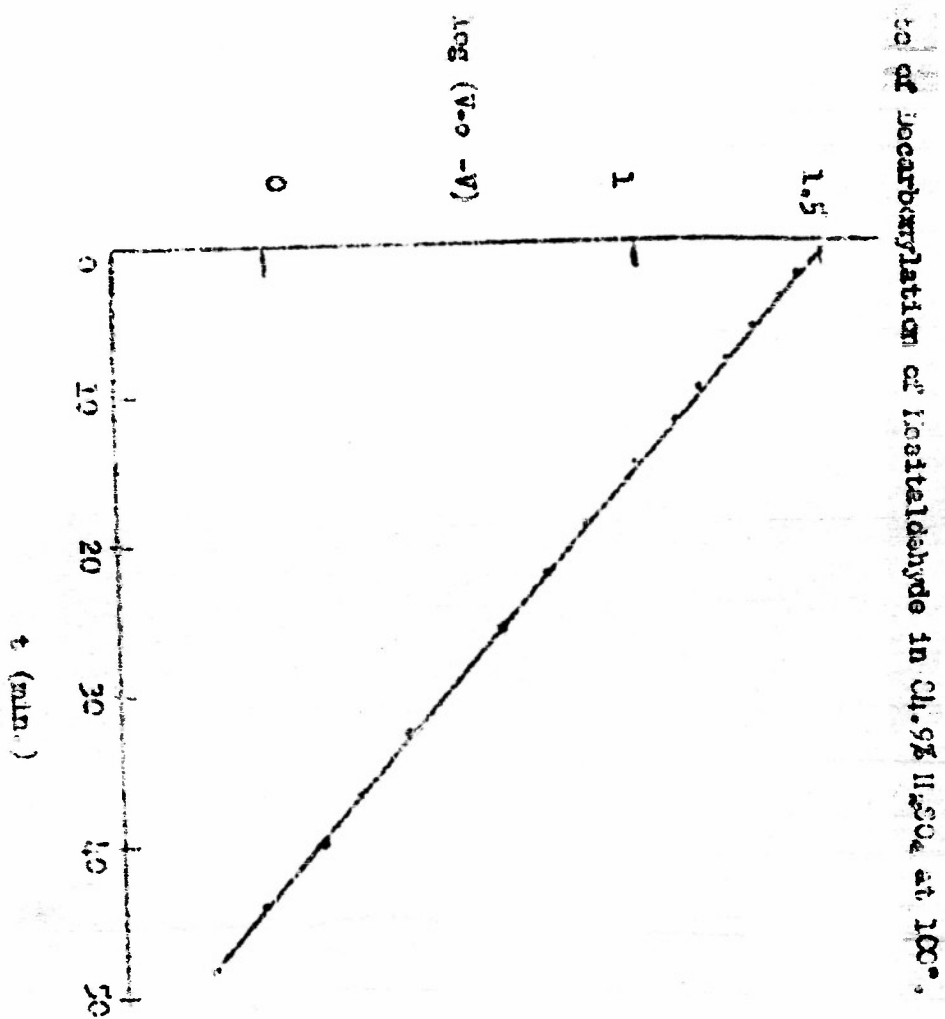


Fig. 2

The Absorption Spectrum of Formaldehyde in Various Percentages H_2SO_4

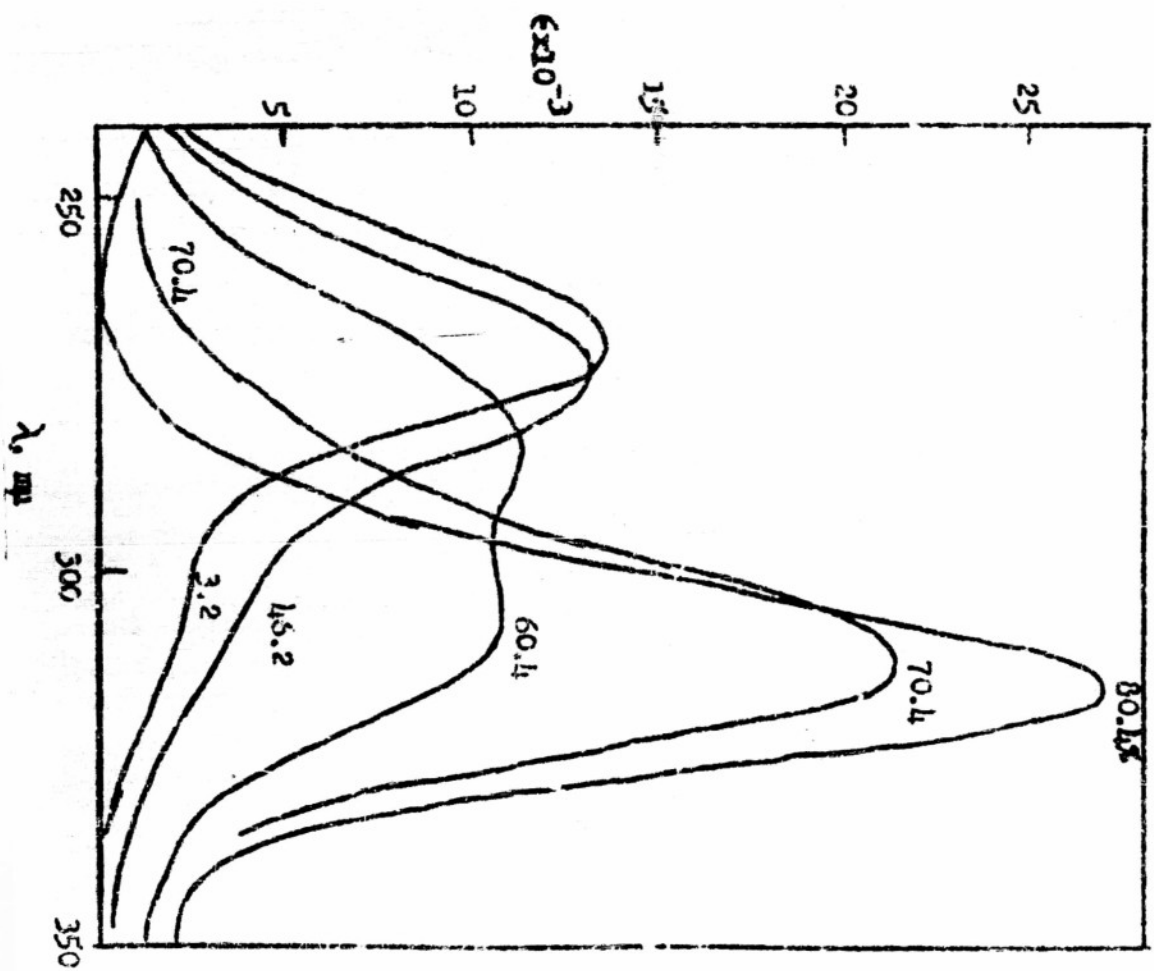


Fig. 3
The Absorption Spectrum of 2,4,6-Triethylbenzaldehyde
in H_2SO_4 at Room Temperature

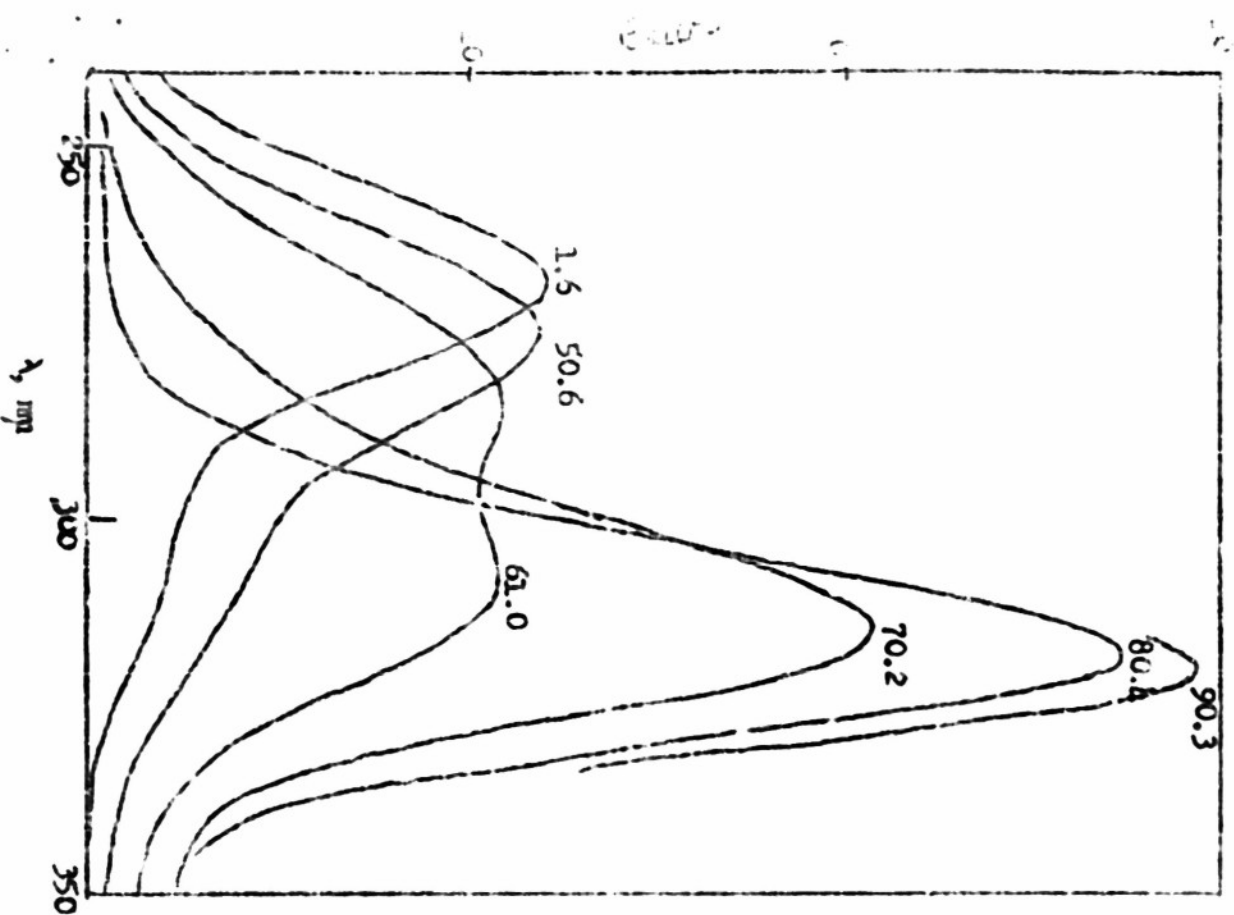
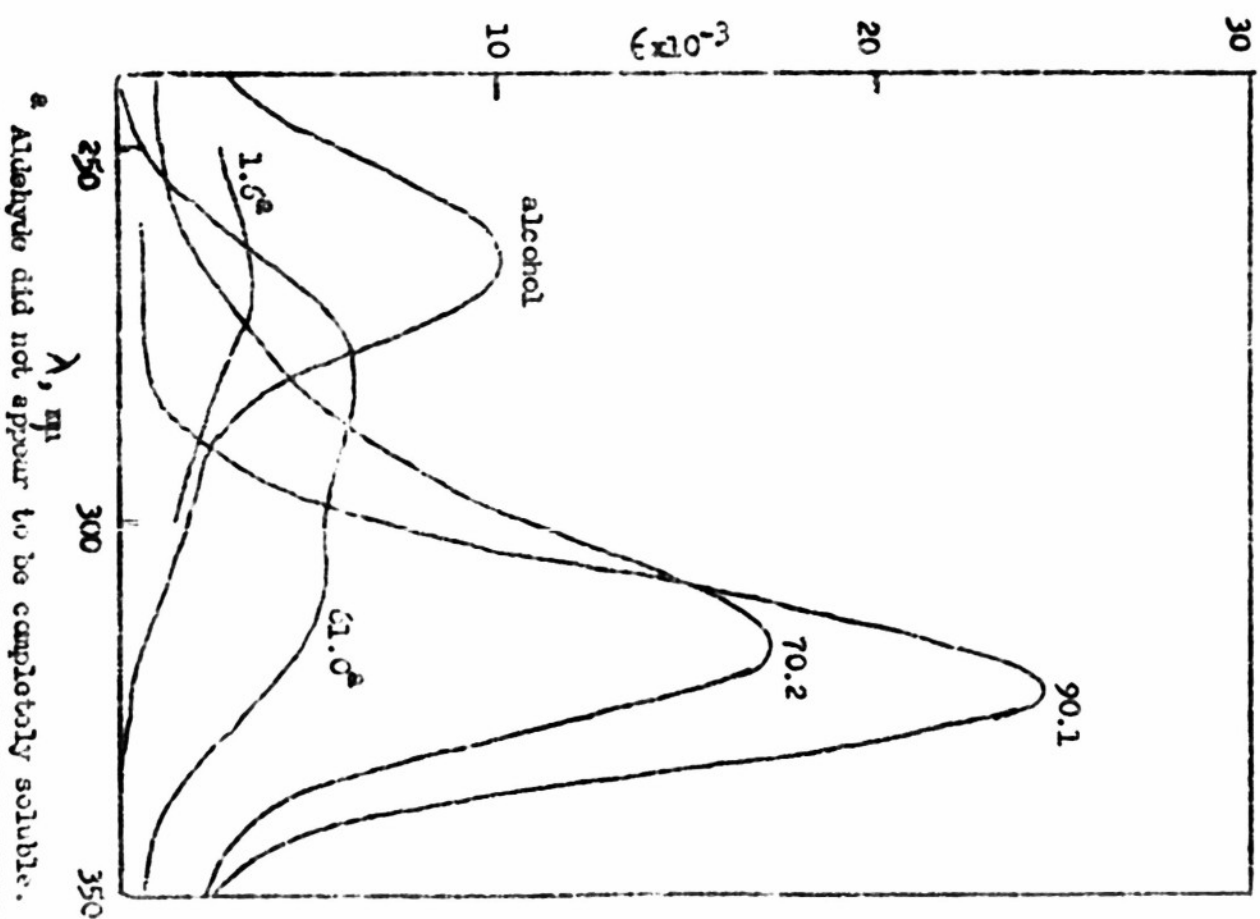


Fig. 4
The Absorption Spectrum of 2,4,6-Trisopropyl-
benzaldehyde in H_2SO_4 at Room Temperature



* Aldehyde did not appear to be completely soluble.

Fig. 5

The Change in Absorption Spectrum with Time of Mesitaldehyde-3-sulfonic acid in 70.2 % H_2SO_4 at 70.0° .

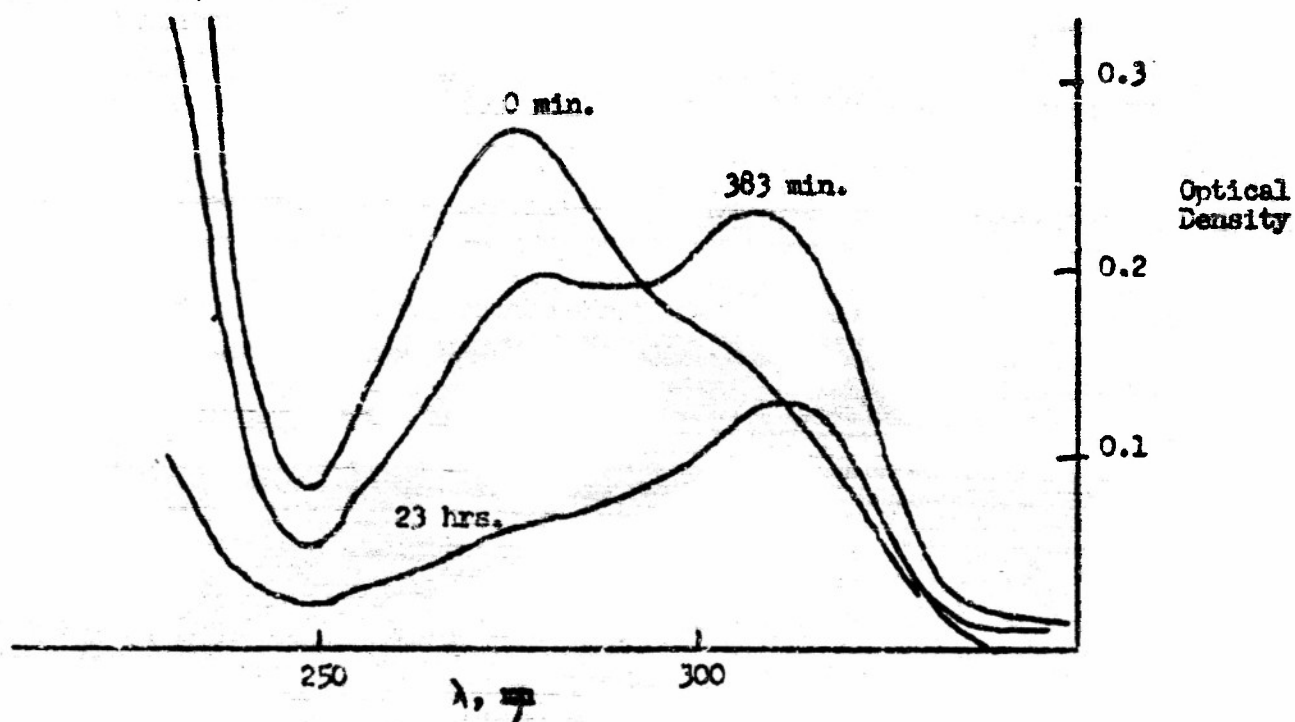


Fig. 6

k versus % Sulfuric Acid

Rate Constants for Decarbonylation of Mesitaldehyde and 2,4,6-Triethylbenzaldehyde at 100° and of 2,4,6-Trisopropylbenzaldehyde at 80° .

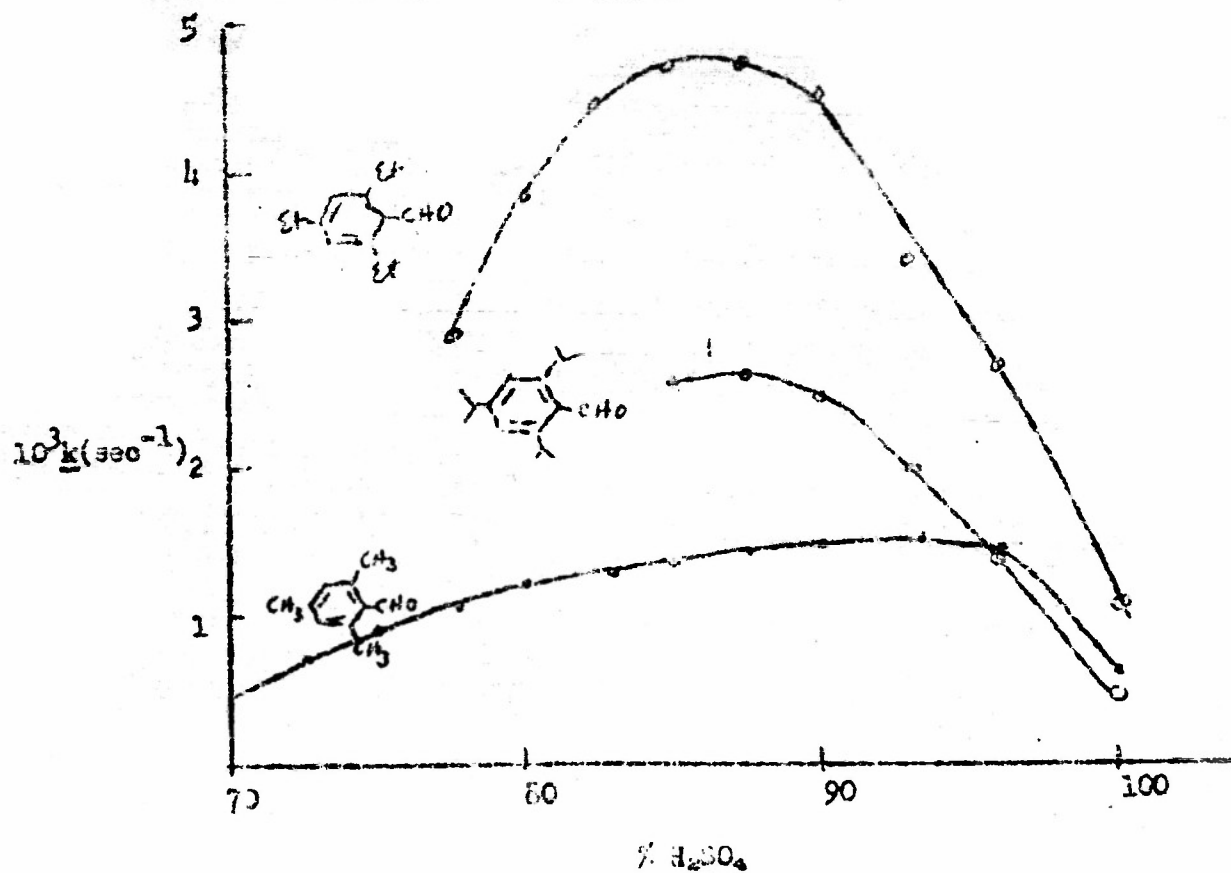


Fig. 7

The Effect of Added Salts on the Rate of Decarboxylation of Mesityldehyde in 100 % H_2SO_4 at $100^\circ C$.

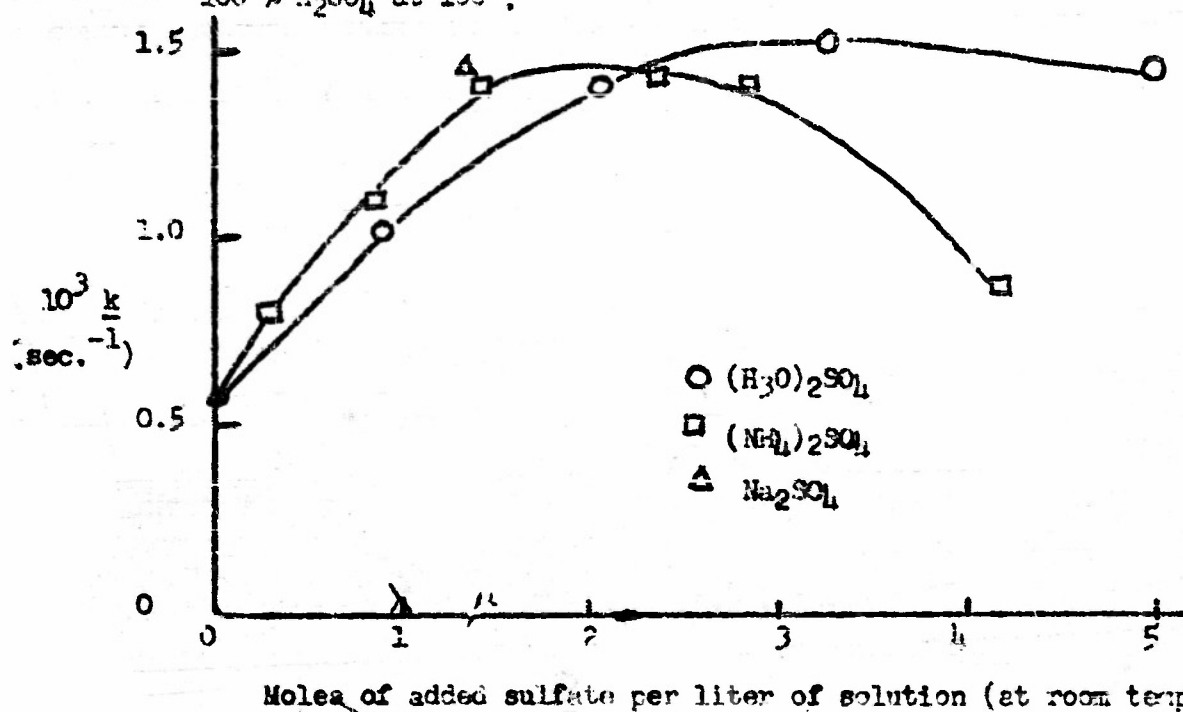


Fig. 8 Activation Energy Plots

