In the case of the cycloalkylideneacetic acids these differences are small, since the controlling factor is the small steric repulsions. The differences for the various cycloalkyl carboxylic acids are also small, since the strain effects are small, but for the cycloalkenyl carboxylic acids the large strain effects due to the endocyclic double bonds produce large changes in the dissociation constants.

Experimental

Preparations of the Acids.—Tiglic acid was prepared by the method of Buckles and Mock,[8] m.p. 64°, from water. β,β-Dimethylacrylic acid was prepared according to Smith,[9] m.p. 67°, from water. Cyclopentylidene,[10] cyclohexylidene-[11] and cycloheptylideneacetic[12] acids were prepared by a Reformatsky reaction with ethyl bromoacetate and the corresponding ketone, followed by saponification and dehydration of the resulting hydroxy ester. Their m.p.'s were 63° (lit. 64°[10]), 91° (lit. 91°[12]), 55° (lit. 54°[12]), respectively.

Cyclobutenecarboxylic acid was prepared from cyclobutanecarboxylic acid,[13] and had m.p. 72° (pentane).

Cyclopentenecarboxylic Acid.—Cyclopentanone (10 g.) and sodium cyanide (12 g., 100% excess) in water (50 ml.) was cooled in an ice–salt bath, and sodium bisulfite (25 g.) in water (60 ml.) added slowly with vigorous stirring during 0.5 hour. After stirring for a further 4 hr. the solution was filtered, and filtrate and residue extracted with ether. The ether solution was dried and the solvent removed under reduced pressure. The crude cyanohydrin in pyridine (25 ml.) and benzene (25 ml.) was treated with a mixture of phosphorus oxychloride (30 ml.) and pyridine (30 ml.). The mixture was warmed slowly and heated under reflux for 0.5 hour. The reaction mixture was cooled and poured onto ice and extracted with ether. The ethereal solution was washed with dilute hydrochloric acid and water, and then dried. Evaporation of the solvent and distillation of the residue gave 1-cyanocyclopentene (6 g.), b.p. 72° (15 mm.), n^{20}_{D} 1.4690. The nitrile was hydrolyzed with 90% phosphoric acid at 130–140° for 5 hours.[14] The cooled mixture was diluted with an equal volume of water and extracted with ether. The ether was dried and evaporated and the residue crystallized from pentane to m.p. 121° (lit. 122°[15]).

Cyclohexenecarboxylic Acid.—Cyclohexanone cyanohydrin was prepared in like manner and dehydrated to 1-cyanocyclohexene, b.p. 86° (18 mm.), n^{20}_{D} 1.4818. The nitrile was hydrolyzed as above to the acid, m.p. 38° from pentane (lit. 37°).[16]

Cycloheptenecarboxylic Acid.—Cyanocycloheptene, b.p. 54–55° (1 mm.), n^{22}_{D} 1.4850, prepared from cycloheptanone as above, was hydrolyzed with phosphoric acid to the acid, m.p. 51° from pentane (lit. 49°[17]).

Determination of Dissociation Constants.—The dissociation constants were determined from the value of the *p*H at the half-neutralization point of a graph of *p*H *vs.* volume of sodium hydroxide solution. The solvent used was prepared by mixing equal volumes of purified dry ethanol and water and had d^{25}_{4} 0.9272. Samples of the acids (0.05–0.10 g.) were dissolved in this solvent (50 ml.) in a beaker immersed in a constant temperature bath (at 25.0 ± 0.2°), and were titrated with carbonate-free sodium hydroxide (0.245 *N*) prepared in the same solvent. The *p*H determinations were with a model G Beckman *p*H meter, using glass and calomel electrodes with long leads, and frequent standardizations were made with buffer solutions of *p*H 4 and 7. The determinations were carried out in duplicate or triplicate. The values were not corrected for ionic strength, or liquid junction potential. The results are shown in the table. Under the same conditions benzoic acid had $K_a\ 10^7 = 5.55$.

Mexico 20, D. F., Mexico

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(12) G. A. R. Kon and C. J. May, *J. Chem. Soc.*, **129**, 1549 (1927).

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(16) E. A. Braude and J. A. Coles, *ibid.*, 2014 (1950).

(17) E. A. Braude, W. F. Forbes and E. A. Evans, *ibid.*, 2202 (1953).

[Contribution from the Department of Chemistry of the University of Washington]

Acid–Base Catalysis in Concentrated Acid Solution. Deuterium Isotope Effects in the Decarbonylation of Aromatic Aldehydes[1]

By W. M. Schubert and Howard Burkett[2]

Received May 16, 1955

Isotope effects have been determined for (1) the decarbonylation of mesitaldehyde *vs.* deuteromesitaldehyde (MesCDO) in 60 to 100% sulfuric acid, and (2) the decarbonylation of mesitaldehyde in 60 to 100% sulfuric *vs.* deuterosulfuric acid. The observed isotope effects are not explained by a termolecular mechanism. With certain reasonable assumptions, a bimolecular mechanism of successive proton transfer steps, equations 2 and 3, is consistent with the isotope effects. All previous observations[5] are explainable on the basis of the bimolecular mechanism, including (1) the shapes of the plots of k_{obsd} *vs.* % sulfuric acid for 2,4,6-trimethyl-, triethyl- and triisopropylbenzaldehyde, and (2) the fact that for the mesitaldehyde decarbonylation, the change in k_{obsd} with sulfuric acid percentage is in apparent agreement with the unimolecular mechanism, 4, over part of the acid range.

Introduction

It was first suggested by Hammett, on the basis of the constancy of the sum,[3] log $k_{obsd} + H_0$, that for many reactions catalyzed in concentrated acids the rate-controlling step is a unimolecular decomposition of a conjugate acid of the substrate (equation 4), or a proton transfer from the conjugate acid to solvent bases, this step being independent of the concentration or nature of the bases which receive the proton.[4] The acid-catalyzed decarbonylation of 2,4,6-trialkylbenzaldehydes has been shown not to proceed by this generalized mechanism, although for mesitaldehyde there is apparent agreement with the unimolecular mechanism over part of the range of sulfuric acid concentrations in which

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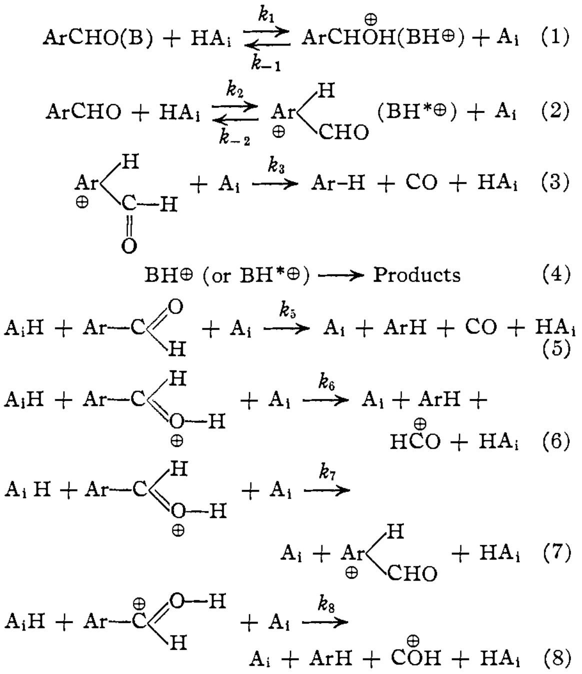
(2) On sabbatical leave from De Pauw University during 1953–1954.

(3) For substrates that are appreciably ionized, the more general equation, $\log k_{obsd} + H_0 - \log([B]/[B]_{stoich}) =$ const., applies; see, *e.g.*, reference 5.

(4) L. P. Hammett "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.

the reaction was studied.[5] The effects of changing mineral acid concentration and of added salts were found to be consistent with either a bimolecular proton transfer (equation 2 or 3) or a termolecular process (equation 5, 6, 7 or 8). In the following equations, the charges on solvent acids and bases, HA_i and A_i, are left unspecified.



$$\mathrm{ArCHO(B)} + \mathrm{HA_i} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ArCH\overset{\oplus}{O}H(BH^{\oplus})} + \mathrm{A_i} \quad (1)$$

$$\mathrm{ArCHO} + \mathrm{HA_i} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\oplus}{\mathrm{Ar}}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown \mathrm{CHO}} \mathrm{(BH^{*\oplus})} + \mathrm{A_i} \quad (2)$$

$$\underset{\oplus}{\mathrm{Ar}}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown \mathrm{C(=O)-H}} + \mathrm{A_i} \xrightarrow{k_3} \mathrm{Ar{-}H} + \mathrm{CO} + \mathrm{HA_i} \quad (3)$$

$$\mathrm{BH^{\oplus}\ (or\ BH^{*\oplus})} \longrightarrow \mathrm{Products} \quad (4)$$

$$\mathrm{A_iH} + \mathrm{Ar{-}C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown \mathrm{H}} + \mathrm{A_i} \xrightarrow{k_5} \mathrm{A_i} + \mathrm{ArH} + \mathrm{CO} + \mathrm{HA_i} \quad (5)$$

$$\mathrm{A_iH} + \mathrm{Ar{-}C}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown\!\!\diagdown \underset{\oplus}{\mathrm{O}}{-}\mathrm{H}} + \mathrm{A_i} \xrightarrow{k_6} \mathrm{A_i} + \mathrm{ArH} + \mathrm{H\overset{\oplus}{C}O} + \mathrm{HA_i} \quad (6)$$

$$\mathrm{A_iH} + \mathrm{Ar{-}C}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown\!\!\diagdown \underset{\oplus}{\mathrm{O}}{-}\mathrm{H}} + \mathrm{A_i} \xrightarrow{k_7} \mathrm{A_i} + \underset{\oplus}{\mathrm{Ar}}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown \mathrm{CHO}} + \mathrm{HA_i} \quad (7)$$

$$\mathrm{A_iH} + \mathrm{Ar{-}C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \overset{\oplus}{\mathrm{O}}{-}\mathrm{H}}{\diagdown \mathrm{H}} + \mathrm{A_i} \xrightarrow{k_8} \mathrm{A_i} + \mathrm{ArH} + \mathrm{\overset{\oplus}{C}OH} + \mathrm{HA_i} \quad (8)$$

In order to delineate the mechanism more specifically, the following modes of attack were undertaken: (1) comparison of the rates for deuteromesitaldehyde (MesCDO) with those for mesitaldehyde in various concentrations of sulfuric acid, and (2) comparison of the rates for mesitaldehyde in deuterosulfuric acid with those in sulfuric acid.

Experimental

Deuteromesitaldehyde (MesCDO).[6]—Mesitil[7] (5.34 g.) was reduced with an equimolecular quantity of lithium aluminum deuteride[8] in anhydrous ether and was recrystallized from methanol. The reduction product (MesCD(OH)CD(OH)Mes), m.p. 204.5–205.3°, was obtained in 85% yield. A solution of this material in dry benzene was shaken for two hours with an equimolecular quantity of freshly recrystallized lead tetraacetate at room temperature. Washing with water, drying the benzene solution over anhydrous sodium sulfate and distilling afforded the deuteromesitaldehyde, b.p. 126–127° (25 mm.), in 64% yield.

High isotopic purity was indicated by infrared spectra. For example, peaks at 3.72 and 3.80 μ, which are strong for mesitaldehyde, are completely absent for deuteromesitaldehyde. The latter has strong peaks at 4.75 and 4.87 μ, which are not present for mesitaldehyde. Mass spectral data (Table I) indicate good isotopic purity and the absence of more than one deuterium atom per molecule.

TABLE I

MASS SPECTRA[a]

Mass No.	MesCHO (p = 17.3 μ)	MesCDO (p = 7.7 μ)
147	1530 ($\mathrm{MesCO^{\oplus}}$)	292 ($\mathrm{MesCO^{\oplus}}$)
148	1101 (Parent compd.)	54[b]
149	108 (Carbon isotope)	197 (Parent compd.)
150	7	16 (Carbon isotope)

[a] Consolidated Engineering Company instrument, Model No. 21-103. [b] The low volatility of mesitaldehyde required the use of high ionization potential (70 v.), sufficient for the removal of hydrogen from the methyl groups. This undoubtedly accounts for the fact that this number is larger than it would be for the carbon isotope of the acylonium ion alone.

Deuterosulfuric Acid.—The apparatus consisted of an inverted U-tube of 22 mm. diameter with a side stopcock and 24/40 standard taper joints at each end. Sulfur trioxide (Sulfan B, Allied Chemical and Dye Corporation) was placed in a flask at one end and an empty flask at the other. After the flask containing sulfur trioxide was thoroughly cooled in an ice-bath, the empty flask was replaced with one containing pure deuterium oxide[9] which was then cooled in ice. The system was evacuated by means of an aspirator with an intervening drying tube containing Drierite and the stopcock closed. Upon being warmed to room temperature the sulfur trioxide evaporated into the cooled deuterium oxide. The evaporation was allowed to continue until the total volume corresponded to a concentration in excess of 100% D_2SO_4. The composition was determined by titration of weighed samples. Solutions for kinetic studies were prepared by suitable dilution with deuterium oxide.

The concentration of all acid solutions was checked by titration of weighed samples.

The preparation of other materials is described in a previous publication.[5]

Kinetic Method.—The spectrophotometric method, using the Beckman DU instrument, for following the reaction rates has been described.[5] The temperature was controlled to ±0.03°.

Results

Aldehyde Basicities.—Mesitaldehyde and deuteromesitaldehyde (MesCDO) have identical basicities in sulfuric acid. The spectra of the two aldehydes, taken at room temperature, are identical within experimental error in several concentrations of sulfuric acid between 59 and 100%, including 64% in which approximately one-half of the aldehyde is in the form of its conjugate acid.

Mesitaldehyde is more completely ionized in deuterosulfuric acid than in sulfuric acid. The ultraviolet spectra of mesitaldehyde in sulfuric acid and in deuterosulfuric acid at room temperature are identical above 85% acid concentration; mesitaldehyde is thus completely ionized to conjugate acid ($BH^{\oplus}$ or $BD^{\oplus}$) in these media. In 70% acid, absorption at 312 mμ (λ_{max} for conjugate acid) was slightly greater in deuterosulfuric acid. The difference was larger in lower acid concentration.[10] The spectra at two acid concentrations are shown in Fig. 1. Table II shows the percentage of mesitaldehyde conjugate acid in several percentages of the two isotopic mineral acids, calculated from the spectra at several wave lengths by the isosbestic point method.[4,11] The fourth column of the table

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(5) W. M. Schubert and Roland E. Zahler, THIS JOURNAL, **76**, 1 (1954).

(6) Analogous to the preparation of deuterobenzaldehyde (C_6H_5-CDO) by K. B. Wiberg, *ibid.*, **76**, 5371 (1954).

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

(8) Obtained from Metal Hydrides Incorporated on allocation from the United States Atomic Energy Commission.

(9) Obtained from Stuart Oxygen Company on allocation from the United States Atomic Energy Commission.

(10) That deuterosulfuric acid appears to be a stronger acid than sulfuric has been noted by other workers and is discussed by R. P. Bell, "Acid–Base Catalysis and Molecular Structure," in "Advances in Catalysis," Academic Press, Inc., New York, N. Y., 1952, Vol. IV, p. 184.

(11) Although the values of percentage conjugate acid have a relatively large error, the ratios of concentrations ($[BD^{\oplus}]/[BH]^{\oplus}$) used to calculate the values in the last column of Table IV were more consistent. Each ratio was calculated at the same wave length for both acids and medium effects are approximately the same in the two mineral acids.

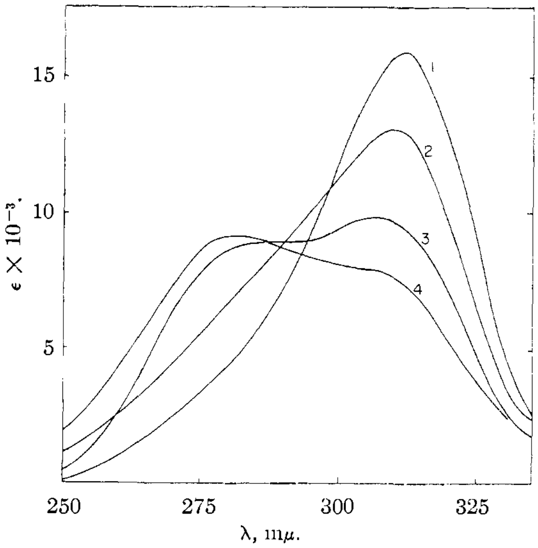

Fig. 1.—Spectra of mesitaldehyde in: (1) 65.02% D_2SO_4; (2) 65.06% H_2SO_4; (3) 58.94% D_2SO_4; (4) 58.88% H_2SO_4.

gives an estimate of the difference in acidity function of the two acids.

TABLE II

Acid, %	Conjugate acid, % in D_2SO_4	Conjugate acid, % in H_2SO_4	$H_{0(D_2SO_4)} - H_{0(H_2SO_4)}$[a]
58.8	42 ± 2	24 ± 3	−0.36
64.0	68 ± 3	49 ± 2	− .35
65.0	74 ± 4	54 ± 3	− .38
70.05	86 ± 4	74 ± 4	− .34

[a] Calcd. using equation $H_{0(D_2SO_4)} - H_{0(D_2SO_4)} = \log ([B]/[BD^{\oplus}]/[B]/[BH^{\oplus}])$.

Rate Results.—For the determination of the rate constants the plot of log $(D - D_\infty)$ *vs.* time was linear within ±0.05 unit of log $(D - D_\infty)$, except for an occasional point. The plot was made at three or more wave lengths for each experiment. In all cases the reaction rate was followed beyond 60% completion and in a few cases beyond 90% completion. For six of the mesitaldehyde experiments duplicate runs were made. The maximum deviation of the rate constants was ±4.5% and the average deviation was ±2.8%.

A comparison of the rates of decarbonylation of mesitaldehyde and deuteromesitaldehyde in sulfuric acid is shown in Table III.

Comparison of the rate constants for the decarbonylation of mesitaldehyde in deuterosulfuric acid and in sulfuric acid is made in Table IV.

Discussion

The Bimolecular Mechanism; the Steady-state Assumption.—The only reasonable bimolecular path has been shown previously to be the successive proton transfer steps 2 and 3.[5] This mechanism is consistent with the deuterium isotope effects and explains nicely all previously observed facts,[5] provided that in low mineral acid percentages (59–70%) step 3 is rate controlling, and in high mineral acid percentages (85–100%) steps 2 and 3 both contribute as rate-controlling steps of comparable velocity.

TABLE III

H_2SO_4, %	$k_{obsd} \times 10^3$ (80°) MesCHO	$k_{obsd} \times 10^3$ (80°) MesCDO	k_{ArCHO}/k_{ArCDO}
100.04	0.083	0.049	1.8
96.31	.192	.070	2.8
85.21	.182	.065	2.8
59.88	.022	.012	1.8

TABLE IV

Acid, % (approx.)	$k_{obsd} \times 10^3$ (80°) H_2SO_4	$k_{obsd} \times 10^3$ (80°) D_2SO_4	Ratio of k_{obsd} $(k_{H_2SO_4}/k_{D_2SO_4})$	$\frac{k_{H_2SO_4}}{k_{D_2SO_4}} \times \frac{[BD^{\oplus}]}{[BH^{\oplus}]}$
99.5	0.091	0.038	2.4	2.4
96	.192	.091	2.1	2.1
85	.182	.119	1.5	1.5
85	.065[a]	.051[a]	1.3[a]	1.3[a]
70	.085	.100	0.85	0.98
65	.054	.075	0.72	1.03
59	.018	.032	0.56	0.98

[a] MesCDO.

The general rate expression for reactions 2 and 3 is given by equation 9. Equation 9 is derived assuming only that the carbon conjugate acid, $BH^{*\oplus}$, is a kinetically unstable intermediate (*i.e.*, in steady-state concentration).[12,13] Activity coefficient terms are omitted for the sake of simplicity.

$$k_{obsd} = \frac{[B]}{[B]_{stoich}} \frac{\Sigma k_2[HA_i]}{1 + \frac{\Sigma k_{-2}[A_i]}{\Sigma k_3[A_i]}} \qquad (9)$$

Ionization to oxygen conjugate acid (equation 1) is nearly complete in 75% sulfuric acid. On the other hand, the species $BH^{*\oplus}$ is never present in spectrally detectable concentration. It is a property of this system that even when ionization to oxygen conjugate acid ($BH^{\oplus}$) is considerable, the velocity of step 2 forward remains slow and never becomes so great as to give $BH^{*\oplus}$ in large concentration.[14,15] This is because the increase in the specific rate constant, k_2, with increasing sulfuric acid percentage, is approximately balanced by a decrease in the concentration of B *via* equilibrium 1. Whether step 2 forward or step 3 is rate-controlling will then depend only on the relative velocities of step 2 *reverse vs.* step 3 (see *e.g.*, ref. 13, pp. 123 ff.)

The Condition $\Sigma k_{-2}[A_i] \ll \Sigma k_3[A_i]$.—Here step 2 is rate controlling and equation 9 reduces to 10. The ratio of k_{obsd} for mesitaldehyde to deuteromesitaldehyde (symbolized as B_D) is given by equation 11.

$$k_{obsd} = \frac{[B]}{[B]_{stoich}} \Sigma k_2[HA_i] \qquad (10)$$

$$\frac{k_{ArCHO}}{k_{ArCDO}} = \frac{[B]}{[B_D]} \frac{\Sigma k_2[HA_i]}{\Sigma k_2^D[HA_i]} \qquad (11)$$

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(12) For a comparable treatment in which a major side equilibrium, such as equation 1, is not involved, see L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2785 (1939); also reference 13, pp. 122–135.

(13) R. P. Bell, "Acid–Base Catalysis," Oxford University Press, London, 1941.

(14) The rate constants for steps 2 forward and reverse are small, of course, compared to the forward and reverse rate constants for the practically instantaneous equilibrium 1. Step 2 involves proton transfer to carbon; step 1, to basic oxygen.

(15) Were the velocity of step 2 forward ever to become so great as to give $BH^{*\oplus}$ in appreciable concentration, first order kinetics would no longer be observed under the condition, equation 9, that $\Sigma k_{-2}[A_i] \sim \Sigma k_3[A_i]$; *cf.* ref. 13, p. 125.

The two aldehydes have experimentally identical basicities, hence $[\mathrm{B}]/[\mathrm{B_D}] = 1$. Furthermore, it is reasonable to assume $k_2 = k_2^{\mathrm{D}}$ for each $\mathrm{HA_i}$ species. Thus, when step 2 is rate controlling there should be no isotope effect when ArCDO is substituted for ArCHO. However, a positive isotope effect is observed throughout the range of sulfuric acid concentration used (Table III). Therefore, the condition $\Sigma k_2[\mathrm{A_i}] << \Sigma k_3[\mathrm{A_i}]$ does not pertain with mesitaldehyde in any of these acid concentrations.

The Condition $\Sigma k_{-2}[\mathrm{A_i}] \gg \Sigma k_3[\mathrm{A_i}]$.—Here step 3 is rate controlling and 2 an established equilibrium. The general rate equation 9 reduces to 12

$$k_{\mathrm{obsd}} = \frac{[\mathrm{B}]}{[\mathrm{B}]_{\mathrm{stoich}}} \frac{\Sigma k_2[\mathrm{HA_i}]\Sigma k_3[\mathrm{A_i}]}{\Sigma k_{-2}[\mathrm{A_i}]} \tag{12}$$

Since

$$\Sigma k_2[\mathrm{B}][\mathrm{HA_i}] = \Sigma k_{-2}[\mathrm{BH}^{*\oplus}][\mathrm{A_i}] \tag{13}$$

equation 12 becomes

$$k_{\mathrm{obsd}} = \frac{[\mathrm{BH}^{*\oplus}]}{[\mathrm{B}]_{\mathrm{stoich}}} \Sigma k_3[\mathrm{A_i}] \tag{14}$$

The ratio of k_{obsd} for mesitaldehyde *vs.* deuteromesitaldehyde in sulfuric acid is given by equation 15. Since in all probability $[\mathrm{BH}^{*\oplus}]/[\mathrm{B_DH}^{*\oplus}]$ is unity[16] and $k_3 > k_3^{\mathrm{D}}$ for each $\mathrm{A_i}$ species, equation 15

$$\frac{k_{\mathrm{ArCHO}}}{k_{\mathrm{ArCDO}}} = \frac{[\mathrm{BH}^{*\oplus}]\Sigma k_3[\mathrm{A_i}]}{[\mathrm{B_DH}^{*\oplus}]\Sigma k_3^{\mathrm{D}}[\mathrm{A_i}]} \tag{15}$$

predicts $k_{\mathrm{ArCHO}}/k_{\mathrm{ArCDO}} > 1$. Such an isotope effect was observed throughout the acid range used (Table III).

The ratio of observed rate constants for mesitaldehyde in sulfuric *vs.* deuterosulfuric acid is given by equation 16. In 59–70% acid, $[\mathrm{BH}^{\oplus}]/[\mathrm{BD}^{\oplus}]$ is less than unity (Table II) and the negative isotope effect in this region can be explained on the basis of $[\mathrm{BH}^{*\oplus}]/[\mathrm{BD}^{*\oplus}]$ likewise being less than unity.[17] The fact that $k_{\mathrm{H_2SO_4}}/k_{\mathrm{D_2SO_4}}$ is experimentally just equal to $[\mathrm{BH}^{\oplus}]/[\mathrm{BD}^{\oplus}]$ (see column 5, Table IV) brings up some interesting points concerning deuterium isotope effects. Unfortunately, lack of space prohibits complete discussion of these points. At any rate, the implication of the equality of $k_{\mathrm{H_2SO_4}}/k_{\mathrm{D_2SO_4}}$ and $[\mathrm{BH}^{\oplus}]/[\mathrm{BD}^{\oplus}]$ in 59–70% acid is that (1) the ratio of oxygen to carbon basicity of mesitaldehyde is the same in deuterosulfuric as in sulfuric acid, and (2) the ratio of the catalytic constants for abstraction of the aldehydic hydrogen, $k_3/k_3^{\mathrm{D_2SO_4}}$, has the value unity.[18]

$$\frac{k_{\mathrm{H_2SO_4}}}{k_{\mathrm{D_2SO_4}}} = \frac{[\mathrm{BH}^{*\oplus}]\Sigma k_3[\mathrm{A_i}]}{[\mathrm{BD}^{*\oplus}]\Sigma k_3^{\mathrm{D_2SO_4}}[\mathrm{A_i}^{\mathrm{D_2SO_4}}]} \tag{16}$$

It has been shown that the condition $\Sigma k_{-2}[\mathrm{A_i}] >> \Sigma k_3[\mathrm{A_i}]$ is in agreement with the observed isotope effects in 59–70% mineral acid. However, this condition cannot pertain in 85–99% acid, for which $k_{\mathrm{H_2SO_4}}/k_{\mathrm{D_2SO_4}}$ is greater than unity.

The Condition $\Sigma k_{-2}[\mathrm{A_i}] \sim \Sigma k_3[\mathrm{A_i}]$.—The rate equation 9 cannot be further simplified unless k_{-2}/k_3 has the same value for each solvent base species. This is considered highly unlikely (see *e.g.*, ref. 12, 13). The velocity depends partly on the actual proton transfers of steps 2 and 3 and partly on the equilibrium 2 controlled by the solvent acid concentrations.[13] A positive isotope effect would be expected in the comparison of ArCHO with ArCDO in sulfuric acid (*i.e.*, $k_{\mathrm{ArCHO}}/k_{\mathrm{ArCDO}} > 1$). A positive isotope effect for mesitaldehyde in sulfuric *vs.* deuterosulfuric acid likewise would be expected (*i.e.*, $k_{\mathrm{H_2SO_4}}/k_{\mathrm{D_2SO_4}} > 1$), when ionization of the substrate is practically complete, as it is in 85–100% acid.

The bimolecular mechanism then is in agreement with the experimental facts if in 59 to 70% mineral acid $\Sigma k_{-2}[\mathrm{A_i}] >> \Sigma k_3[\mathrm{A_i}]$ (*i.e.*, step 3, rate controlling) and in 85 to 99% $\Sigma k_{-2}[\mathrm{A_i}] \sim \Sigma k_3[\mathrm{A_i}]$ (*i.e.*, step 2 forward and step 3 of comparable velocity). Such a changeover in the relative magnitudes of $\Sigma k_{-2}[\mathrm{A_i}]$ and $\Sigma k_3[\mathrm{A_i}]$ means that step 2 reverse is slowed more than step 3 as the proportion of basic species effective in these steps is changed from more water and less bisulfate ion to less water and more bisulfate ion, *i.e.*, that $k_{-2(\mathrm{H_2O})}/k_{3(\mathrm{H_2O})} > 1$ and $k_{-2(\mathrm{HSO_4^{\ominus}})}/k_{3(\mathrm{HSO_4^{\ominus}})}$ have a value around unity or less. Such a possibility is reasonable. For example, step 2 reverse with bisulfate ion as the base obviously would be subject to considerably greater steric strain (relative to water as the base) in the transition state than would step 3.

A continued gradual decrease in the ratio $\Sigma k_{-2}[\mathrm{A_i}]/\Sigma k_3[\mathrm{A_i}]$ as the population of effective solvent basic species is shifted toward bisulfate ion means that step 2 will become more and more rate controlling, and step 3 less rate controlling, with increased mineral acid percentage. Thus, the increase in $k_{\mathrm{H_2SO_4}}/k_{\mathrm{D_2SO_4}}$ observed between 85 and 99% (Table IV) is explained. The fact that $k_{\mathrm{H_2SO_4}}/k_{\mathrm{D_2SO_4}}$ is smaller for deuteromesitaldehyde than for mesitaldehyde in 85% mineral acid (Table IV) would be due to step 2 being less rate controlling for deuteromesitaldehyde because of the decreased velocity of step 3. The changing magnitude of $k_{\mathrm{ArCHO}}/k_{\mathrm{ArCDO}}$ (Table III) also is explained similarly provided that the isotope effect with bisulfate ion in step 3 is larger than with water.

Consideration of Fig. 2.—The contours of the curves of k_{obsd} *vs.* per cent. sulfuric acid (Fig. 2) for trimethyl-, triethyl- and triisopropylbenzaldehyde are completely consistent with the bimolecular mechanism. Analysis of the shapes of these curves is more conveniently made in terms of equation 18, obtained from equation 17 and the general rate equation 9.

$$[\mathrm{B}][\mathrm{HA_i}] = K_{\mathrm{i}}^{\mathrm{BH}^{\oplus}}[\mathrm{BH}^{\oplus}][\mathrm{A_i}] \tag{17}$$

$$k_{\mathrm{obsd}} = \frac{[\mathrm{BH}^{\oplus}]}{[\mathrm{B}]_{\mathrm{stoich}}} \frac{\Sigma k_2 K_{\mathrm{i}}^{\mathrm{BH}^{\oplus}}[\mathrm{A_i}]}{1 + \dfrac{\Sigma k_{-2}[\mathrm{A_i}]}{\Sigma k_3[\mathrm{A_i}]}} \tag{18}$$

For mesitaldehyde the increase in k_{obsd} between 60 and 75% sulfuric acid means that the increase in $[\mathrm{BH}^{\oplus}]/[\mathrm{B}]_{\mathrm{stoich}}$ is the governing factor in the

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(16) The aldehydes ArCHO and ArCDO have the same oxygen basicity; there is no reason to believe they would not have the same carbon basicity.

(17) For a discussion and examples of a pre-equilibrium between catalyst and substrate being responsible for a negative isotope effect see, *e.g.*, reference 13, pp. 145–148.

(18) There appears to be no example in the literature in which the catalytic constants of light and heavy water toward *proton abstraction* have been measured. However, the hydrolysis of methyl chloride proceeds at the same rate in light or heavy water, indicating that for this process $\mathrm{H_2O}$ and $\mathrm{D_2O}$ have the same "catalytic constant"; C. G. Swain, R. Gardinaud and A. D. Ketley, THIS JOURNAL, **77**, 934 (1955).

change in over-all rate constant. In 75 to 100% acid $[BH^{\oplus}]/[B]_{stoich}$ is unity (*i.e.*, ionization to $BH^{\oplus}$ practically complete) and a gradual decrease in $\Sigma k_{-2}[A_i]/\Sigma k_3[A_i]$ apparently is such that the decreases in numerator and denominator of equation 18 approximately balance each other over a goodly part of this range, giving near agreement with the predictions of a unimolecular mechanism (dotted line, Fig. 2). Finally, in the highest sulfuric acid concentration (95–100%) the numerator will be decreasing more rapidly than the denominator (*i.e.*, the denominator is approaching the limiting value of unity as $\Sigma k_{-2}[A_i]$ becomes sufficiently smaller than $\Sigma k_3[A_i]$) and a decrease in over-all rate constant is observed.

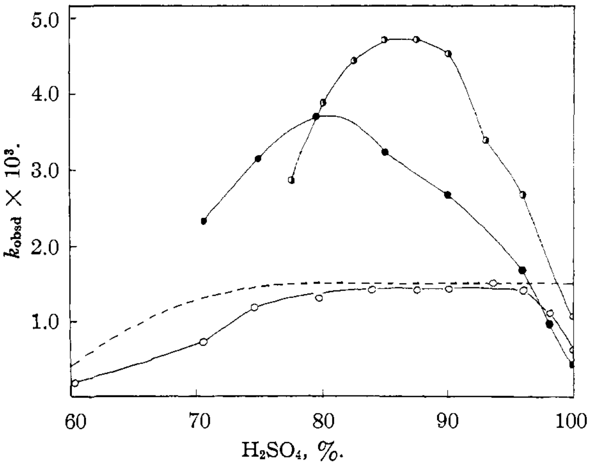

Fig. 2.—Change in k_{obsd} with % H_2SO_4: O, mesitaldehyde at 100.0°; ◑, 2,4,6-triethylbenzaldehyde at 100.0°; ●, 2,4,6-triisopropylbenzaldehyde at 80.0°; ---, theoretical unimolecular k_{obsd} calculated for equation 4.

For triisopropylbenzaldehyde, ionization to $BH^{\oplus}$ is practically complete in 80% sulfuric acid (pK_a = −5.1, ref. 5) and k_{obsd} would reach a maximum at about this point. The quantity $\Sigma k_{-2}[A_i]/\Sigma k_3 \cdot [A_i]$ should be decreasing more rapidly with increasing acid percentage (*i.e.*, with decreasing water to bisulfate ion ratio) than for mesitaldehyde. This would be due to the greater increase in steric strain in the transition state for step 2 reverse (compared to step 3) with bisulfate ion as compared to water as the base. The result should be a sharper maximum in k_{obsd} and a more rapid decrease in k_{obsd} in higher acid percentages, as found. For triethylbenzaldehyde, the curve, Fig. 2, should be intermediate between that for mesitaldehyde and that for triisopropylbenzaldehyde, also as found.

Termolecular Mechanisms.—Conceivable termolecular mechanisms are given by equations 5 through 8. Mechanism 5 predicts $k_{H_2SO_4} > k_{D_2SO_4}$ for mesitaldehyde in all sulfuric acid concentrations and therefore does not account for the fact that $k_{H_2SO_4}$ is less than $k_{D_2SO_4}$ in 59–70% acid (Table IV). Mechanism 6 cannot account for the fact that $k_{H_2SO_4}/k_{D_2SO_4}$ is experimentally equal to $[BH^{\oplus}]/[BD^{\oplus}]$ in 59–70% acid (Table IV) since $k_{6(H_2SO_4)}$ should be greater than $k_{6(D_2SO_4)}$. Furthermore one would not expect k_{ArCHO} to be greater than k_{ArCDO} (Table III). Mechanism 7 can be rejected on the same grounds. Mechanism 8 is inconsistent with the observed isotope effects since it requires that $\Sigma k_{8(H_2SO_4)}[HA_i][A_i]$ be equal to $\Sigma k_{8(D_2SO_4)}[DA_i][A_{iD_2SO_4}]$ in 59 to 70% acid (although proton *vs.* deuteron transfer is involved) but not in higher per cent. acid.

No termolecular mechanism accounts for the isotope effects in 59–70% acid. It is still conceivable, though not considered likely, that the bimolecular mechanism with step 3 rate-controlling, shown to prevail in 59–70% acid, changes to a termolecular mechanism (*i.e.*, equation 5) at higher acid percentages.

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Acid Dissociation Constants and Rates of Saponification for 2-Furoic and β-2-Furyl-, β-2-Thienyl- and β-1-Naphthylacrylic Acids

BY CHARLES C. PRICE[1] AND EDWARD A. DUDLEY

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The rate of saponification of ethyl 2-furoate is considerably slower than predicted from the pK_a for the acid, similar to previous observations[2] for 2-thenoic and 1-naphthoic acids. This effect disappears in the three corresponding β-arylacrylic acids. The data indicate a stereospecific acid strengthening factor, for 2-thenoic and 2-furoic acids and it is suggested that this factor may be chelate hydrogen bonding.

In an earlier report,[2] it was pointed out that the esters of several 1-naphthoic and 2-thenoic acids all saponified at a rate slower than predicted from the Hammett expression relating the rate of saponification of various substituted[3] benzoic acids to the dissociation constants. Since the course of saponification, involving expansion of the carboxyl carbon from trigonal to tetrahedral, would impose considerable steric demands compared to the simple removal of a proton in dissociation, it was proposed that this effect was some sort of steric hindrance to the saponification process.

The source of such a steric hindrance for the case of ethyl 1-naphthoate is quite obvious since this ester is, in effect, an *ortho*-substituted benzoate. For ethyl 2-thenoate one would have to presume

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(2) C. C. Price, E. C. Mertz and J. Wilson, THIS JOURNAL, **76**, 5131 (1954).

(3) The relationship fails frequently for *ortho*-substituted benzoic acids due to steric effects superimposed on the electrical effects normally involved in correlations following the Hammett equation.