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

Aromatic Electrophilic Substitution by Hydrogen. V. Ionization Equilibria and Kinetics of the Acid-catalyzed Decarboxylation of 2,4,6-Trimethoxybenzoic Acid and its Methyl Ester[1]

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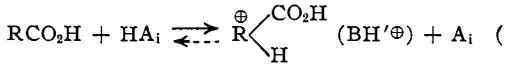
The ionization of 2,4,6-trimethoxybenzoic acid and the kinetics of its decarboxylation were determined by an ultraviolet spectroscopic method. The acid ionization constant is 2.6×10^{-4}. Ionization to $RCO^{\oplus}$ is complete in 64% perchloric acid. Spectral changes in 20–47% perchloric acid can be interpreted as (1) representing ionization to $RCO_2H_2^{\oplus}$, or (2) possibly being due to an unusual medium effect, on RCO_2H. If there is appreciable ionization to $RCO_2H_2^{\oplus}$ in 47% acid, then the rate-controlling step appears to be bi- or termolecular.[2a,2b] On the other hand, if there is no appreciable $RCO_2H_2^{\oplus}$, then the Hammett unimolecular rate equation is obeyed. Methyl 2,4,6-trimethoxybenzoate has a pK_a^B of −4.5. It forms $RCO^{\oplus}$ slowly in 60% perchloric acid and rapidly in 80% sulfuric acid.

The acid-catalyzed decarbonylation of 2,4,6-trialkylbenzaldehydes and decarboxylation of 2,4,6, trialkylbenzoic acids have been shown recently not to proceed by the Hammett unimolecular path 3-at least in media in which ionization of substrate species to conjugate acid (equilibrium of type 1) is appreciable.[2a,2b] A bi- or termolecular process such as 4, 5, 6, or 7 prevails (HA_i = any solvent acid and A_j = any solvent base, the charges not being designated).

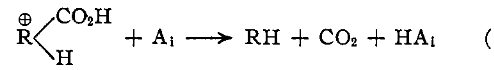
$$RCO_2H(B) + HA_i \rightleftharpoons RCO_2H_2^{\oplus}(BH^{\oplus}) + A_i \quad (1)$$

$$RCO_2H_2^{\oplus} \rightleftharpoons RCO^{+} + H_2O \quad (2)$$

$$RCO_2H_2^{\oplus} \text{ (or other conjugate acid, } BH'^{\oplus}) \longrightarrow RH + CO_2 + H^{\oplus} \quad (3)$$



$$RCO_2H + HA_i \rightleftharpoons \overset{\oplus}{R}\begin{matrix}CO_2H\\H\end{matrix} \ (BH'^{\oplus}) + A_i \quad (4)$$



$$\overset{\oplus}{R}\begin{matrix}CO_2H\\H\end{matrix} + A_i \longrightarrow RH + CO_2 + HA_i \quad (5)$$

$$HA_i + RCO_2H + A_j \longrightarrow A_i + RH + CO_2 + HA_j \quad (6)$$

$$HA_i + RCO_2H_2^{\oplus} + A_j \longrightarrow A_i + RH + CO_2H^{\oplus} + HA_j \quad (7)$$

The role of solvent acid and base species in a reaction of this type is probably best studied under conditions in which ionization of the substrate to conjugate acid is practically complete. This becomes clear on examination of the rate expression 8 for a bimolecular process (4 or 5) or the rate expression 9 for termolecular process 6.[2a]

$$k_{\text{obsd}} = \frac{[BH^{\oplus}]}{[B] + [BH^{\oplus}]} \sum_{i} k_i[A_i] f_{BH^{\oplus}}/f_{ts_i} \quad (8)$$

$$k_{\text{obsd}} = \frac{[BH^{\oplus}]}{[B] + [BH^{\oplus}]} \sum_{ij} k_{ij}[HA_i][A_j] f_{HA_i} f_{A_j} f_{BH^{\oplus}}/f_{tr_{ij}} \quad (9)$$

When ionization to $BH^{\oplus}$ is nearly complete, k_{obsd} is directly proportional to the quantity under the summation sign. On the other hand, when ionization to $BH^{\oplus}$ is slight, the quantity $[BH^{\oplus}]/([B] + [BH^{\oplus}])$ is changing very rapidly with acid concentration and the determination of this quantity is subject to fairly large error. Naturally, even when ionization to $BH^{\oplus}$ is large, the activity coefficient terms of equation 8 or 9 must be properly treated before conclusions can be made about the effect of concentration of solvent acid or base species.

A study of the decarboxylation of 2,4,6-trimethoxybenzoic acid was undertaken with the expectation that ionization to $RCO_2H_2^{\oplus}$ would be complete in low mineral acid concentration. Barring appreciable acylization (equilibrium 2), the conjugate acid then might be the main substrate species over a wide range of acid concentration and the role of solvent acid and base species perhaps more readily discernible.

Experimental

Materials.—Methyl 2,4,6-trimethoxybenzoate, m.p. 69–70° from aqueous methanol, and 2,4,6-trimethoxybenzoic acid, m.p. 142–143° dec. from aqueous methanol, were prepared by the method of Holmes, White and Wilson.[3]

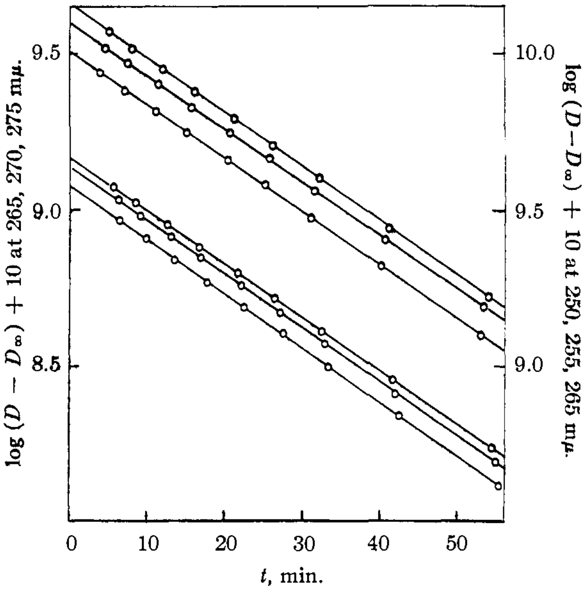


Fig. 1.—First-order plot, decarboxylation of 2,4,6-trimethoxybenzoic acid in 10.3% $HClO_4$ at 20.0°. Starting at the bottom and progressing upward the lines are for wave lengths 250, 255, 260, 275, 270 and 265 mμ, respectively.

Perchloric acid solutions were prepared by dilution of C.P. 60% perchloric acid, sulfuric acid solutions by dilution of C.P. concentrated acid. The acid strengths were determined by titration against standard sodium hydroxide.

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[1] Supported in part by the Office of Naval Research.

[2] (a) W. M. Schubert and Roland E. Zahler, THIS JOURNAL, 76, 1 (1954); (b) W. M. Schubert, Jere Donohue and J. D. Gardner, *ibid.*, 76, 9 (1954).

[3] P. Holmes, D. E. White and I. H. Wilson, *J. Chem. Soc.*, 2810 (1950).

Decarboxylation Products.—A 0.2-g. sample of 2,4,6-trimethoxybenzoic acid when shaken for 10 minutes at 40° with 10 ml. of 59.5% sulfuric acid (presaturated with carbon dioxide) gave a 97% yield of carbon dioxide as determined in the gasometric apparatus previously described.[2b] The reaction mixture when diluted with water yielded 1,3,5-trimethoxybenzene, m.p. 50–52°, no depression in m.p. with an authentic sample.

Ionization of 2,4,6-Trimethoxybenzoic Acid and its Methyl Ester in Perchloric Acid.—Spectra of 2,4,6-trimethoxybenzoic acid were measured in several strengths of perchloric and sulfuric acid. Spectra were determined at −10 to −15° and extrapolated to zero time for media in which the decarboxylation reaction is very rapid. Because of the insolubility of the trimethoxy acid at the low temperature, stock solutions were made up in alcohol and then a 2-ml. aliquot diluted to 100 ml. with perchloric acid. Some of the spectra are plotted in Fig. 2. Spectra of methyl 2,4,6-trimethoxybenzoate were taken at 10°. These are plotted in Fig. 3.

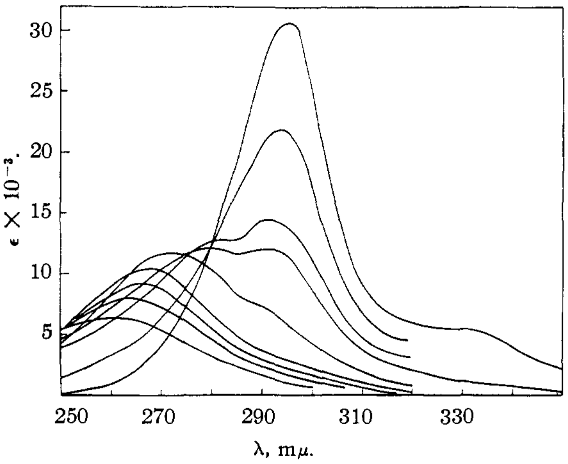

Fig. 2.—Zero time spectra of 2,4,6-trimethoxybenzoic acid in various concentrations $HClO_4$ at −15°. Beginning with lowest curve (at 290 mμ) and progressing upward, the percentages $HClO_4$ are: 5, 19.8, 29.7, 35.3, 47.5, 50.2, 52.1, 54.5 and 63.9. The spectrum in 69.3 and 79.4% H_2SO_4 is essentially same as in 63.9% $HClO_4$.

Spectrophotometric Determination of K_a.—Equation 8 was used to calculate the ratio $[RCO_2\ominus]/[RCOOH]$ for 2,4,6-trimethoxybenzoic acid from the ultraviolet spectrum in water, 0.0010 and 0.010% perchloric acid. The spectrum in 0.08 *N* sodium hydroxide was taken as that of pure $RCO_2\ominus$. The spectrum in 1.93% perchloric acid was taken as that of pure RCO_2H. Because of slow decarboxylation the latter spectrum was extrapolated to zero time from a first-order plot of log $(D - D_\infty)$ against time. The zero time spectrum did not change measurably in 1.93 to 5.3% perchloric acid. All the curves passed through an isosbestic point at about 245 mμ. The spectral data are given in Table I. Values of $[RCO_2\ominus]/[RCO_2H]$ and of the equilibrium constant, K_a, are given in Table II. Equation 9 was used to calculate K_a. The activity coefficient of the undissociated acid, f_{RCO_2H}, was assumed equal to unity. The product $f_{H\oplus}f_{RCO_2\ominus}$ was assumed unity except in 0.010% perchloric acid, where it was assigned the value 0.98. The quantity α is the degree of dissociation and c is the stoichiometric concentration, 9.78×10^{-5} mole/liter.

$$\frac{[RCO_2\ominus]}{[RCO_2H]} = \frac{\epsilon_{RCO_2H} - \epsilon}{\epsilon - \epsilon_{RCO_2\ominus}} \tag{8}$$

$$K_a = \frac{[RCO_2\ominus]\,[H\oplus]}{[RCO_2H]}\,\frac{f_{H\oplus}f_{RCO_2\ominus}}{f_{RCO_2H}} = \frac{(\alpha c)(\alpha c + [HClO_4])}{c(1 - \alpha)}\,\frac{f_{H\oplus}f_{RCO_2\ominus}}{f_{RCO_2H}} \tag{9}$$

Kinetic Method.—The apparatus and method previously described were used.[2a] Rate constants were obtained by following the change in optical density at several wave lengths of a solution of 2,4,6-trimethoxybenzoic acid (5 to 20×10^{-5} molar depending on the intensity of the spectrum). Wave lengths were chosen in which the spectral change was large (*i.e.*, 250 to 300 mμ). Figure 1 shows a first-order plot of one run, which is typical of reactions that were not extremely fast. The constants obtained under such conditions are presumed reliable within 2–3%. In the very fast runs (*i.e.*, in 39.0 and 49.1% perchloric acid at 10°) the points were scattered and may be in error by as much as 10%. In Table III are shown the rate constants obtained under various conditions.

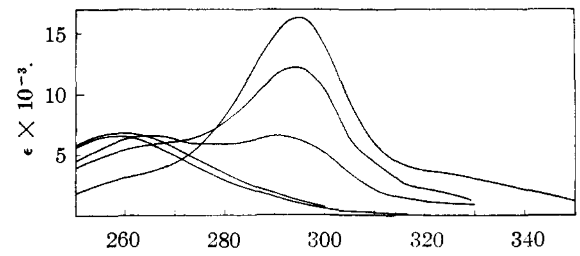

Fig. 3.—Spectra of methyl 2,4,6-trimethoxybenzoate in various concentrations $HClO_4$ at 10°. Beginning with lowest curve (at 290 mμ) and progressing upward the percentages $HClO_4$ are: 1.0, 41.9, 55.6, 58.6 and 60.0 (the last percentage at −10°).

TABLE I

ACID IONIZATION OF 2,4,6-TRIMETHOXYBENZOIC ACID. VALUES OF $\epsilon \times 10^{-3}$ IN VARIOUS MEDIA

	Media				
λ, mμ	0.08 *N* NaOH	H_2O[a]	0.001% $HClO_4$[a]	0.01% $HClO_4$[a]	1.93% $HClO_4$[b]
240	5.35	5.10	4.82	4.32	4.04
245	4.60	4.59	4.56	4.56	4.54
250	3.72	4.06	4.37	5.00	5.34
255	2.81	3.49	4.11	5.39	6.07
260	2.05	2.96	3.77	5.44	6.31
265	1.54	2.50	3.38	5.09	6.07
270	1.23	2.08	2.82	4.33	5.17
275	0.96	1.62	2.20	3.36	4.05
280	.63	1.15	1.59	2.48	2.99
285	.27	0.69	1.05	1.77	2.13
290	.10	0.42	0.70	1.22	1.48

[a] Concentration of trimethoxybenzoic acid, 9.78×10^{-5} *M*. [b] Measured at 10° and extrapolated to zero time.

TABLE II

VALUES OF $[RCO_2\ominus]/[RCO_2H]$ AND K_a

	$[RCO_2\ominus]/[RCO_2H]$			
Medium	260 mμ	270 mμ	280 mμ	$K_a \times 10^4$
Water	3.70	3.64	3.54	2.78 ± 0.08
0.0010% $HClO_4$	1.49	1.48	1.46	2.34 ± .02
0.010% $HClO_4$[a]	0.262	0.271	0.276	2.64 ± .08
			Av.	2.59

[a] The product $f_{H\oplus}f_{RCO_2\ominus}$ assumed equal to 0.98, near the value of the mean ionic activity coefficient of hydrochloric acid in 0.001 molal solution.[4]

Discussion

Ionization of 2,4,6-Trimethoxybenzoic Acid as a Base.—Zero time spectra (Fig. 2) of the carboxylic acid in perchloric acid were measured at −15° because of the rapid rate of decarboxylation at higher temperature. Between 1 and 5% perchloric acid the spectrum remains unchanged except for a

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(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 547.

TABLE III

RATE CONSTANTS FOR THE DECARBOXYLATION OF 2,4,6-TRIMETHOXYBENZOIC ACID

Acid, %	$10^3 k$ (sec.$^{-1}$) at 10.0°	Acid, %	$10^3 k$ (sec.$^{-1}$) at 10.0°
10.3 $HClO_4$	0.213, 0.218	18.2 H_2SO_4	0.94
19.9 $HClO_4$	0.80, 0.79	39.4 H_2SO_4	Fast
29.6 $HClO_4$	2.8, 2.7	58.8 H_2SO_4	Fast
39.0 $HClO_4$	9.1, 9.2	10.1 HCl	1.20
49.8 $HClO_4$	*ca.* 17	19.3 HCl	12
59.7 $HClO_4$	0.68. 0.67		

slight lateral medium shift.[5] The spectrum in 5% perchloric acid is undoubtedly that of free RCO_2H. The spectrum in 64% perchloric acid is probably that of the acylonium ion, $RCO^\oplus$. This is inferred from the great intensity of the peak and the shoulder at about 330 mμ (features found in the spectrum of mesitoylacylonium ion[6,2b]) as well as the slow rate of decarboxylation in 63.9% perchloric acid. The question remains whether there is present any appreciable concentration of intermediate conjugate acid, $RCO_2H_2^\oplus$, between 5 and 63.9% perchloric acid. The following features of the spectrum may indicate the presence of $RCO_2H_2^\oplus$; (1) the approximate doubling in intensity and shift to longer wave length of the principal absorption peak from 5 to about 30% perchloric acid is about what would be expected for at least partial ionization to $RCO_2H_2^\oplus$ in this region; (2) starting in about 35% and continuing to say 52% perchloric acid there is a broadening of the spectrum and a splitting into two peaks. This is accompanied by a growth of the peak that appears at longer wave lengths; (3) the change in ϵ is greater between 47.5 and 63.9% (*i.e.* more intensely absorbing $RCO^\oplus$ coming in) than between 5 and 47.5% perchloric acid; (4) the shoulder at 330 mμ is absent in the medium strengths of mineral acids; and (5) there appear to be two isosbestic points, one around 250 mμ and the other around 280 mμ, although the exact location of isosbestic points is complicated by the medium shift.[5] An alternative interpretation is that the change in spectrum between 5 and 47% perchloric acid is the result of an unusual medium shift on RCO_2H,[7] and that little or no conjugate acid is present in any medium.

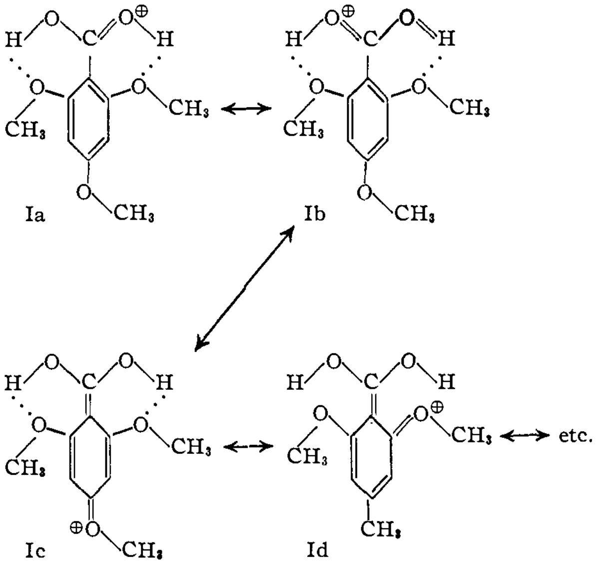
A reasonably constant value of $pK_a{}^B = -0.9$ was calculated for equilibrium 1 by least squares solution[5] of equation 10 using spectral data in up to 32% perchloric acid, assuming no $RCO^\oplus$ in this region. A more erratic value of 0.7 for $\log K_{BH^\oplus}$ of equilibrium 2 was calculated by means of equation 11.[2b] Spectral data in greater than 50% perchloric acid were used, assuming no RCO_2H present.

$$pK_a{}^B + \epsilon_{BH^\oplus}\left(\frac{h_0}{\epsilon_B - \epsilon}\right) - \left(\frac{h_0}{\epsilon_B - \epsilon}\right) = 0 \quad (10)$$

$$-\log K_{BH^\oplus} = \log \frac{[BH^\oplus]}{[Ac^\oplus]} \log a_{H_2O} \quad (11)$$

The values of $pK_a{}^B$ and $-\log K_{BH^\oplus}$ obtained are probably at best only approximate in view of the following facts: (1) if there are two ionization steps, they overlap each other considerably; (2) the peaks for the three species, RCO_2H, $RCO_2H_2^\oplus$ and $RCO^\oplus$, lie close together; (3) the spectra are extrapolated to zero time, the rapidity of the decarboxylation reaction being a source of error even at −15°; and (4) some solutions contained 2% of ethanol because of the limited solubility of the substrate. The value −0.9 for $pK_a{}^B$ is probably too high. Thus if the spectrum of $RCO_2H_2^\oplus$ has about the same intensity as the spectrum of the conjugate acid of the methyl ester (see discussion below concerning the ester), that is, about 16,000, then formation of $RCO_2H_2^\oplus$ would appear to be about half complete in 35% perchloric acid. This would make the value of $pK_a{}^B$ about −1.5. In unpublished work in these laboratories by H. W. Burkett, it has been found that 2,4,6-trimethoxybenzaldehyde, without benefit of as much hydrogen bond stabilization of the conjugate acid as in $RCO_2H_2^\oplus$ (Ia–Id), is almost completely ionized in 47% perchloric acid and has a $pK_a{}^B$ of −1.9.

In any event, 2,4,6-trimethoxybenzoic acid appears to be a strong oxygen base. The conjugate acid of trimethoxybenzoic acid is stabilized by increased resonance interaction (over that in the free base) of the protonated carboxyl group with the methoxyl substituents, assuming no large steric inhibition of resonance. Moreover, there may be added hydrogen bond stabilization of the conjugate acid as exemplified in the resonance structures Ia, Ib, Ic and Id.[8]



The 2,4,6-trimethoxybenzoyl ion also should be stabilized considerably by resonance (this would not be damped sterically), much more than 2,4,6-

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(5) L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935).

(6) M. S. Newman and N. C. Deno, *ibid.*, **73**, 3652 (1951).

(7) Medium effects previously observed[5,12] are small lateral shifts only. The referee has pointed out that the change observed here could be the result of a medium effect on the internal hydrogen bond of the carboxylic acid.

(8) It is unlikely that the conjugate acid present in largest amount has the proton on an ether oxygen since such a conjugate acid would not be resonance stabilized. In this connection, 1,3,5-trimethoxybenzene does not begin to be ionized to conjugate acid until about 45% perchloric acid.

trimethylbenzoyl ion, for example. However, if the conjugate acid, $ArCO_2H_2^{\oplus}$, is stabilized by hydrogen bonding with respect to $ArCO_2H$, it also is thus stabilized with respect to the acylonium ion. In the ionization of triarylcarbonols to $Ar_3C^{\oplus}$, there is definitely no detectable amount of conjugate acid, $Ar_3COH_2^{\oplus}$ formed.[9] In this case, the resonance stabilization of the conjugate acid is much less than that of the triarylmethylcarbonium ion.

Ionization of 2,4,6-Trimethoxybenzoic Acid as an Acid.—As an acid, 2,4,6-trimethoxybenzoic acid was found to have a K_a of 2.6×10^{-4}. It is thus a much weaker acid than 2,4,6-trihydroxybenzoic acid for which $K_a = 2.8 \times 10^{-2}$.[10] The stabilization of 2,4,6-trihydroxybenzoate ion by hydrogen bridging involving the hydrogen on the *ortho* hydroxy groups is, of course, not carried over to the anion of the trimethoxy acid. For a similar reason, salicylic acid ($K_a = 1.05 \times 10^{-3}$) is a much stronger acid than *o*-methoxybenzoic acid ($K_a = 8.2 \times 10^{-5}$) although the *meta* (or *para*) hydroxy and methoxybenzoic acids are of approximately equal strength.[11]

Kinetics of the Decarboxylation of 2,4,6-Trimethoxybenzoic Acid.—The original objective of examining the kinetics of a reaction in which $[BH^{\oplus}]$ is practically constant over a wide range of mineral acid concentration was not achieved due to the occurrence of the acylization equilibrium 2. The acylization makes the rate data much more difficult to interpret. The decline in k_{obsd} beyond 50% perchloric acid (Table III) is no doubt due, at least principally, to the formation of acylonium ion by equilibrium 2. The rate data below 47% perchloric acid can be interpreted in either of two ways depending upon whether the change in zero time spectrum with changing mineral acid concentration is interpreted as representing ionization or a medium shift on un-ionized B.

The modified Hammett equation 12, derived for equation 3 with the reasonable assumption that $(f_B f_{BH^{\oplus}})/f_B f_{tr^{\oplus}}) = $ constant, is used as a test for the unimolecular mechanism.[12,13]

$$\log k_{obsd} + H_0 - \log \frac{[B]}{[B]_{stoich}} = \text{const.}$$
$$[B]_{stoich} = [B] + [BH^{\oplus}] + [Ac^{\oplus}] \quad (12)$$

If the spectral changes of Fig. 2 in up to 47% perchloric are due only to medium effects on the free carboxylic acid, then in this region $[BH^{\oplus}]$ and $[Ac^{\oplus}]$ are negligible and $[B]_{stoich} = [B]$. With this assumption, the sum of equation 12 is reasonably constant (see column4 , Table IV). If, on the other hand, the spectral changes up to 47% acid represent ionization (largely to conjugate acid, with some overlapping acylonium ion formation) then equation 12 is not constant. It shows increasing deviation from constancy beyond 20% perchloric acid, where presumed ionization becomes increasingly noticeable. In Table IV are given values of the sum of equation 12 for $pK_a^B = -0.9$ and $pK_a^B = -1.5$, ignoring $[Ac^{\oplus}]$.

TABLE IV

CONSTANCY OF SUM OF EQUATION 12

Acid, %	H_0	log k_{obsd}	Sum[a]	Sum[b]	Sum[c]
10.3 $HClO_4$	−0.16	−3.67	−3.83	−3.76	−3.81
19.9 $HClO_4$	−0.76	−3.10	−3.86	−3.62	−3.79
29.6 $HClO_4$	−1.39	−2.56	−3.95	−3.33	−3.70
39.0 $HClO_4$	−1.84	−2.04	−3.88	−2.67	−3.38
49.8 $HClO_4$	−3.06	−0.77[d]	−3.8[d]	−1.66[d]	−2.5[d]
18.2 H_2SO_4	−0.76	−3.03	−3.79	−3.55	−3.72
10.1 HCl	−0.98	−2.92	−3.90	−3.55	−3.81
19.3 HCl	−1.90	−1.92	−3.92	−2.78	−3.37

[a] Assuming $[BH^{\oplus}]$ and $[Ac^{\oplus}]$ negligible. [b] Assuming $pK_a^B = 0.9$ and ignoring $[Ac^{\oplus}]$. [c] Assuming $pK_a^B = -1.5$ and ignoring $[Ac^{\oplus}]$. [d] Approximate value, since k_{obsd} uncertain (see Table III).

Based on the assumption that there is appreciable ionization to $BH^{\oplus}$ below 47% perchloric acid, k_{obsd} is increasing faster than required by the unimolecular mechanism, and a bi- or termolecular mechanism (4, 5, 6 or 7) may prevail. The behavior of 2,4,6-trimethoxybenzoic acid would then parallel that found for the decarbonylation of 2,4,6-trialkylbenzaldehydes and the decarboxylation of 2,4,6-trialkylbenzoic acids.[2a,b] If the reaction is bimolecular (4 or 5), it cannot be one of specific oxonium ion catalysis ($HA_i = H_3O^{\oplus}$ only, or $A_i = H_2O$ only). As shown by Zucker and Hammett, above about 15% perchloric acid the change in k_{obsd} with increasing mineral acid percentage for an oxonium ion catalysis mechanism is even less than for the unimolecular mechanism.[12,14] For the bimolecular mechanism 4 or 5 to explain a faster rate of increase of k_{obsd} with mineral acid percentages than for the unimolecular mechanism it is necessary only that the perchlorate ion catalysis term of equation 13 make a noticeable but not excessive contribution.[15] We believe it possible that the balance between the first and second terms in brackets of equation 13 could be such as to give apparent agreement with the unimolecular mechanism in up to 20% perchloric acid.

$$k_{obs} = \nu/[B]_{stoich} = \frac{[BH^{\oplus}]}{[B]_{stoich}} \sum_{i} k_i A_i f_{BH^{\oplus}} f_{A_i}/f_{tr_i} =$$
$$\frac{[BH^{\oplus}]}{[B]_{stoich}} k[_{H_2O}[H_2O] f_{BH^{\oplus}} f_{H_2O}/f_{tr^{\oplus}} + k_{ClO_4^{\ominus}}[ClO_4^{\ominus}] f_{BH^{\oplus}} f_{ClO_4^{\ominus}}/f_{tr}] \quad (13)$$

A plot of log *k* (at 10, 20 and 30°) against $1/T$ for the decarboxylation in both 10.3 and 59.7% perchloric acid gave excellent straight lines. From this was obtained an activation energy of 18.4 kcal. in 10.3% acid and 20.6 kcal. in 59.7% acid. The apparent entropies of activation were −12.4 e.u. in 10.3% acid and −2.1 e.u. in 59.7% acid. Since the activation energies and entropies are not pure (*i.e.*, contain heats and entropies of equilibria) and the mechanism of the reaction is not definitely established, interpretation of the values or com-

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(9) V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

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

(11) G. E. K. Branch and D. L. Yabroff, *ibid.*, **56**, 2568 (1934).

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

(13) W. M. Schubert and H. K. Latourette, THIS JOURNAL, **74**, 1829 (1952).

(14) L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939).

(15) For the derivation of the rate expression 13 from equation 4 or 5 see ref. 2a.

parison with those from similar reactions will be deferred.

Behavior of Methyl 2,4,6-Trimethoxybenzoate.—Examination of the spectrum of the methyl ester in perchloric acid at 10° (Fig. 3) show it to be essentially unchanged between 2 and 41.9% perchloric acid. There is presumably no ionization in this region and thus the methyl ester appears to be a weaker base than the corresponding carboxylic acid. In greater than 42% and up to 58.6% acid only a single ionization step is apparent. Although the new peak appears at about the same wave length as the peak for $RCO^{\oplus}$, this cannot be ionization to $RCO^{\oplus}$ in view of the following fact: the rate of decline of the spectrum in 52.9, 55.6 and 58.6% perchloric acid at 10° is extremely slow, much slower than for the carboxylic acid in the same medium at the same temperature. If the ester were appreciably converted to $RCO^{\oplus}$ (either directly or *via* hydrolysis to the acid) during the measurement of the spectrum, instant equilibration with rapidly decarboxylated species would have occurred.[16] The change in spectrum with acid percentage in this region thus must correspond to ester conjugate acid formation.[17] In 60.0% perchloric acid at 10° there is a slow induction period in the rate of spectral change. The rate then increases appreciably but does not follow first-order kinetics and does not attain the rate of decline in spectrum of the carboxylic acid in the same medium. The final spectrum is that of 1,3,5-trimethoxybenzene. Ionization to acylonium ion therefore does occur in 60% acid but it is slow, and is incomplete at the first spectral reading (ϵ = 19.14 at 295 mμ). The decline in spectrum is a consequence of rapid equilibration of the $RCO^{\oplus}$ formed with $RCO_2H_2^{\oplus}$ and RCO_2H followed by decarboxylation. A spectrum taken in 60% perchloric acid at −10° (Fig. 3, ϵ = 16.38 at 295 mμ) did not change with time and is presumed to contain no acylonium ion. In 80% sulfuric acid the spectrum is very intense and the same at first reading as that of the carboxylic acid in the same medium. The rate of decline of this spectrum is the same as for the carboxylic acid. Therefore, in 80% sulfuric acid, the ester has been converted rapidly and completely to acylonium ion.

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[16] Reversal of the equilibrium $RCO_2CH_3H^{\oplus} \rightleftarrows RCO^{\oplus} + CH_3OH$ would be negligible due to the low concentration of methanol compared with water.

[17] Whereas $RCO_2CH_3H^{\oplus}$ and $RCO^{\oplus}$ have about the same λ_{max} although the intensities differ greatly, the presumed $RCO_2H_2^{\oplus}$ has a lower λ_{max} (Fig. 2) than does $RCO^{\oplus}$.

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

The Effect of Ring Strain on the Ultraviolet Spectra of α,β-Unsaturated Carbonyl Compounds

BY W. M. SCHUBERT AND W. A. SWEENEY[1]

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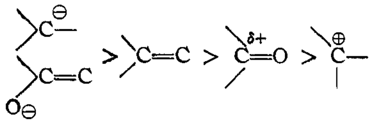
A qualitative correlation has been made of λ_{max} values for α,β-unsaturated carbonyl compounds in which there is strain in one part of the chromophore. The excitation energy has been found to be lower for compounds in which the electron displacement in the spectrally excited state is away from a site of strain; it is generally greater for compounds in which the electron displacement is toward a site of strain.

The following general rule is enunciated to correlate and explain the effect of ring size on the λ_{max} values for the E-band (excitation to a state with greater contribution of dipolar forms[2]) of compounds such as listed in Table I. If a conjugated chromophore is "strained" in one part, then excitation to a dipolar type excited state will occur at longer wave length (lower energy) relative to the corresponding unstrained molecule if electron displacement in the excited state is away from the region of strain. Conversely, absorption will occur at a shorter wave length if displacement is toward that region. This rule can be expected to hold only when the chromophores being compared have the same configuration and in the absence of appreciable steric inhibition of conjugation.

One fundamental assumption of the rule is that during excitation of a chromophore by light absorption, there is no time for the movement of nuclei. This assumption, though often overlooked, is involved in the Franck-Condon principle and is commonly invoked.[3] It is then presumed that removal of electrons from a site of strain in the excitation by light decreases the strain energy in the excited state over that in the ground state. Conversely, addition of electrons to a site of strain increases the strain energy in the excited state over that of the ground state. Care must be exercised in comparing relative ultraviolet excitation energies with rate or equilibrium data. In the latter instances, a re-orientation of atomic nuclei, both in the reacting molecules and surrounding solvent, can take place from ground to transition state or final state.

The basic assumption that the difference in energy between a "strained" and unstrained molecule decreases as the electrons are removed from the site of strain has a corollary. This is that the energy required for a certain angular displacement of attached bonds decreases in the following order



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[1] Proctor and Gamble Fellow, 1952–1953.

[2] See, *e.g.*, K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

[3] See *e.g.*, N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).