General Acid Catalysis in the Dehydration of 1-Aryl-2-phenylethanols[1,2]

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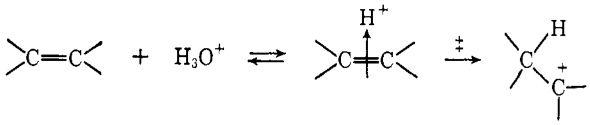
Abstract: The same mechanism of acid-catalyzed dehydration has been observed for *ortho*-, *meta*-, and *para*-substituted 1-aryl-2-phenylethanols in aqueous sulfuric acid containing 5% ethanol and in perchloric acid in 60:40 (v/v) dioxane–water at 25°. General acid catalysis has been observed in the dehydration of 1-(2,4,6-trimethoxyphenyl)-2-phenylethanol with 1:1 dichloroacetic acid–sodium dichloroacetate buffers in "60% dioxane." From this fact it has been deduced that hydration of *trans*-stilbenes and isomerization of *cis*-stilbenes, as well as the dehydration of 1-aryl-2-phenylethanols, proceed by direct, rate-determining proton transfers; the data do not require the intermediacy of π complexes in the reaction schemes in highly aqueous media.

The application of the Zucker–Hammett hypothesis[4] to the study of the mechanism of the hydration of simple olefins by Taft and his coworkers[5] signaled the start of a period of intensive investigation of the mechanism of protonation of carbon–carbon multiple bonds. Early work[6] seemed to suggest the generality of a protonation scheme in which π complexes, reversibly formed from the proton and unsaturated molecule, collapse to carbonium ion in the rate-determining step (eq 1). Not only the Zucker–Hammett hypothesis, but also solvent isotope effects,[7] entropies of activation,[5] and the lack of any demonstrated general acid catalysis[8] seemed to be in accord with sequence 1. In recent years, however, these mechanistic criteria have been reexamined. The Zucker–Hammett hypothesis, as stated by Long and Paul,[4b] has been under scrutiny for a number of years.[9,10] A number of investigators[2,11–15] have presented both theoretical and experimental evidence that solvent isotope effects in multiple bond protonation reactions will vary with the degree of proton transfer in the transition state. Similarly the theory of the mixed solvent isotope effect (Gross–Butler formulation) was considered for an ASE2 (direct proton transfer) mechanism by Gold[16] and his findings are neatly summarized by Kresge[17] in the conclusion that Gross–Butler theory cannot be used as a criterion of mechanism but can provide useful information about reactions whose mechanisms are known. Gold and Kessick[18] extrapolated mixed solvent isotope effects in the hydration of isobutylene to 100% deuterium content using the new theory, and obtained a (k_{H_2O}/k_{D_2O}) value of 1.45 for this reaction, a number of somewhat higher than that found by Purlee and Taft[7] for this reaction. Matesich[19] has shown that the entropy of activation varies with free energy of activation for reactions in which proton transfer to carbon–carbon multiple bonds is the rate-determining step, and has concluded that different protonation mechanisms need not be advanced for the reactions of two different compounds on the basis of differences in entropy of activation, if the compounds differ widely in reactivity. A pertinent case is the fit of data for hydration of isobutylene to Matesich's free energy–entropy correlation.



(1)

The observation of general acid catalysis in the protodetritiation of 1,3,5-trimethoxybenzene-2-*t* by Kresge and Chiang[20] was an important result in the elucidation of the mechanism of protonation of carbon–carbon multiple bonds; this work also pointed to the necessity of further studies, in the low-acidity region, of carbon–carbon multiple bond protonation reactions. In recent years, general acid catalysis has been observed in a number of reactions in which protonation of carbon–carbon multiple bonds is rate determining; most of these investigations have been reported during the course of the present study. The observation of general acid catalysis in protodetritiations and protodedeuteration reactions of aromatic systems is well established;

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[2] Previous paper: D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Org. Chem.*, **33**, 4260 (1968).

[3] National Institutes of Health Predoctoral Fellow, 1966–1968 (GM-32822).

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[6] See, for example: (a) R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *ibid.*, **77**, 1584 (1955); (b) V. Gold and D. P. N. Satchell, *J. Chem. Soc*, 3622 (1955); (c) P Riesz, R. W. Taft, Jr., and R. H. Boyd, *J. Amer. Chem. Soc.*, **79**, 3724 (1957).

[7] E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956).

[8] F. G. Ciapetta and M. Kilpatrick, *ibid.*, **70**, 639 (1948); the source of the inconsistency in these results and those reported here is the method of detection of general acid catalysis by these workers, which depends on the accurate evaluation of the dissociation constant of dichloroacetic acid, an acid of moderate strength, in water. Such an evaluation is a notoriously difficult task; *cf.*, G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 366.

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this phenomenon has been observed in isotope exchange reactions of benzene,[20] azulene,[21,22] and indole[23] derivatives. Protonation reactions of vinyl ethers,[24–26] ethynyl ethers,[27,28] ethynyl thioethers,[28,29] and enamines[30] are general acid catalyzed. The fact that enolizations of ketones show general catalysis[31] strongly suggests that the reverse ketonization reactions involving rate-determining protonation of enols are general acid catalyzed. Cleavage of allylmercury compounds,[32] hydration of styrenes,[33] and hydration of phenylacetylenes[34] are further examples of rate-determining proton transfer reactions showing general acid catalysis.

General acid catalysis in a multiple bond protonation requires general base catalysis in the microscopic reverse step, deprotonation of a carbonium ion to yield olefin. Conversely, the study of a reaction whose rate-determining step is carbonium ion deprotonation provides useful information about the mechanism of the reverse reaction, whose rate-determining step is multiple bond protonation. With the exception of studies of enolization reactions, few (if any) examples of studies exist in which carbonium ion deprotonation is rate determining.

Recently, Noyce, Hartter, and Miles[35] presented evidence that strongly suggested that the isomerization of *cis*-stilbene is another example of a reaction in which carbon–carbon multiple bond protonation is the rate-determining step. Concurrently, Noyce, Hartter, and Pollack[36] showed that the dehydration of 1,2-diphenylethanol, an intermediate in the isomerization sequence, proceeded also *via* a rate-determining proton transfer from carbonium ion to solvent. The ultimate test of the nature of the proton transfer steps in these reactions, and further verification of the mechanistic proposals set forth in these papers, is to be found in the observation of general catalysis in these reactions. We wish to report the observation of general acid catalysis, or more correctly, specific acid–general base catalysis in the dehydration of 1-(2,4,6-trimethoxyphenyl)-2-phenylethanol.

Experimental Section[37]

1-(2,4,6-Trimethoxyphenyl)-2-phenylethanol. 1,3,5-Trimethoxybenzene was prepared by the method of Birch, Clarke-Lewis, and Robertson.[38] A 500-ml, round-bottomed, β-necked flask was equipped with a gas inlet, mechanical stirrer, and a condenser protected with a drying tube. Dry ether (75 ml) was introduced into the flask, followed by *ca.* 20 g of freshly fused $ZnCl_2$. 1,3,5-Trimethoxybenzene (16.8 g) and 17.6 g of distilled, dry phenylacetonitrile were placed in the flask; the entire mixture was stirred and cooled in an ice–water bath, and HCl gas was bubbled at a moderate rate into the flask. A light pink gum was formed after a few minutes, and after *ca.* 4 hr of continued stirring and HCl introduction, this material had formed a solid precipitate; after 7.5 hr, the precipitate was collected, washed several times with ether to remove excess phenylacetonitrile, freed of ether in a nitrogen stream, and placed in 1 l. of H_2O which was refluxed for about 2 hr. The mixture was cooled and extracted several times with 20-ml portions of ether; the ether extracts were washed with three 150-ml portions of 5% sodium carbonate solution and three 100-ml portions of water. The ether extracts were dried ($MgSO_4$), decolorized, and concentrated to yield an oil which crystallized upon addition of a little 95% ethanol. This material was recrystallized from 3:1 ethanol–water, affording 17.3 g (60%) of **2,4,6-trimethoxyphenyl benzyl ketone** as long white prisms, mp 71.8–72.3° (lit.[39] 72°). The material had spectra and elemental analysis consistent with the desired structure. Lithium aluminum hydride reduction of this ketone afforded a 95% yield of **2,4,6-trimethoxyphenylbenzylcarbinol** which was recrystallized from mixed hexanes to mp 63.8–64.5°. This material was pure by thin layer chromatography on Silica Gel G. The ir spectrum of this material showed strong OH-stretch absorbance and was free of bands in the 1680–1750-cm^{-1} (carbonyl region and the 950–990-cm^{-1} (*trans*-olefin) region. The 60-MHz nmr spectrum showed signals at δ_{CDCl_3} (parts per million (ppm) downfield from TMS) 3.1 (2 protons, AB of an ABX pattern, attributed to methylene protons), 3.7 (11 protons, 2 singlets in a ratio of 2:1, attributed to the methoxy protons, and a broad superimposed signal, attributed to the hydroxyl and methine hydrogens), 6.05 (2-proton singlet, attributed to the protons of the substituted phenyl ring), and 7.2 (broad 5-proton singlet, attributed to the unsubstituted phenyl ring protons). *Anal.* Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.58; H, 6.86.

1-(2,4-Dimethoxyphenyl)-2-phenylethanol was prepared by a route exactly analogous to that used for the 2,4,6-trimethoxy analog. In the synthesis of **2,4-dimethoxyphenyl benzyl ketone**, HCl addition was continued for 9 hr. Hydrolysis and work-up were carried out as described previously, yielding, after recrystallization from methanol, a 60% yield of white prisms, mp 46.3–46.8° (lit. 46.5–47°,[40] 47–48°[41]). The desired carbinol, prepared by lithium aluminum hydride reduction, was obtained as an oil which crystallized on standing several weeks. This material could then be recrystallized from mixed hexanes, mp 42–44°. The ir spectrum was very similar to that of the 2,4,6-trimethoxy analog. Signals in the 60-MHz nmr spectrum were at δ_{CDCl_3} 2.6 (1 proton, broad singlet, assigned to hydroxyl proton), 2.8 (2 protons, octet, AB of ABX assigned to methylene protons), 3.6 (6 protons, 2 singlets, assigned to methoxyl protons), 4.9 (1-proton multiplet, X of ABX, assigned to methine proton), 6.3–6.5 and 7.1 (3 protons, multiplet characteristic of 1,2,4-aromatic substitution, assigned to ring protons in the substituted phenyl ring), and 7.2 (5 protons, broad singlet, assigned to unsubstituted phenyl ring protons). *Anal.* Calcd for $C_{16}H_{18}O_3$: C, 74.41; H, 7.02. Found: C, 74.17; H, 7.17.

Monosubstituted 1-aryl-2-phenylethanols were synthesized conventionally by the reaction of benzylmagnesium chloride with the appropriate benzaldehyde in ether. Coupling of the Grignard

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reagent could be reduced to 1 or 2% by the use of a 0.5 *M* excess of magnesium, and by employing concentrations of Grignard reagent of <0.5 *M*. The crude products either crystallized directly from mixed hexanes, or crystallized after partial purification by column chromatography on silica gel. The ir spectra of all carbinols were consistent with the proposed structures. The nmr spectra of all *ortho*-substituted carbinols (except for the *o*-methyl analog) showed ABX signals for the alkyl protons, a broad singlet absorbance for the hydroxyl proton, and appropriate aromatic proton absorption (*cf.* spectrum of the 2,4-dimethoxy analog, above). The spectra of the *o*-methyl and all *meta*- and *para*-substituted analogs studied both here and in previous work[42] showed ($CDCl_3$) 2-proton doublets for the methylene protons at about δ 2.8, 1-proton broad singlets for hydroxyl protons at a variable (usually δ 2–3) chemical shift, 1-proton triplets for methine protons at about δ 5, and appropriate aromatic proton and substituent proton signals.

1-(2-Methoxyphenyl)-2-phenylethanol had mp 67.0–67.8°. *Anal.* Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.63; H, 6.99.

1-(2-Methylphenyl)-2-phenylethanol had mp 48.0–49.5°. *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.59. Found: C, 84.63; H, 7.68.

1-(2-Fluorophenyl)-2-phenylethanol had mp 39.3–41.0°. *Anal.* Calcd for $C_{14}H_{13}FO$: C, 77.76; H, 6.06. Found: C, 77.46; H, 5.99.

1-(4-Fluorophenyl)-2-phenylethanol had mp 45.9–46.9°. *Anal.* Calcd for $C_{14}H_{13}FO$: C, 77.76; H, 6.06. Found: C, 77.46; H, 6.10.

***trans*-2,4,6-Trimethoxystilbene** was synthesized by the method of Seus[43] using diethyl benzylphosphonate (Aldrich), sodium methoxide (Matheson), dry dimethylformamide, and 2,4,6-trimethoxybenzaldehyde[44] on a 0.05-mol scale. The reaction time was 5 hr. Upon dilution of the reaction mixture with water, no precipitate formed. The entire reaction mixture after dilution with water, was extracted with three 50-ml portions of ether, and the combined ether extracts were washed with three 75-ml portions of 10% sodium carbonate solution and ten 75-ml portions of water (to remove dimethylformamide). The ether solution was decolorized (Nuchar), dried ($MgSO_4$), and concentrated to yield 8.1 g (60%) of a light yellow solid, which was recrystallized twice from aqueous ethanol to mp 64.7–65.0° (lit.[45] 57°). *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.68; H, 6.61.

The nmr spectrum was consistent with the proposed structure, but it was not particularly definitive. The ir spectrum contained a band at 970 cm^{-1} (*trans*-olefin), and there were no bands attributable to carbonyl containing impurities. The uv spectrum displayed λ_{max} (60:40 (v/v) dioxane–water) 325 mμ (ϵ 33,000 ± 600).

Kinetic Procedures. Dehydrations of mono-*ortho*-substituted 1-aryl-2-phenylethanols in the "5% ethanol"-H_2SO_4 solvent system[36] were followed by observing the appearance of the appropriate *trans*-stilbene spectrophotometrically at 25.00 ± 0.02° in a manner analogous to that described previously.[36] Beckman uv cells (10.0 cm) were used, however, because of the low solubility of several of the products. Despite this precaution, the starting concentration of 1-(2-fluorophenyl)-2-phenylethanol had to be lowered to 1.3 $\times 10^{-6}$ *M* in order to maintain product solubility. This measure resulted in a total absorbance change for the entire reaction of only 0.3; however, good, reproducible first-order kinetics were obtained. Pseudo-first-order rate constants were determined as the slope of the best straight line drawn visually through a plot of ln ($A_\infty - A_t$) *vs.* time, where A_∞ is the absorbance after ten half-lives, and A_t is the absorbance at time *t*. About 30 points per run were taken. The acidity (wt % H_2SO_4) of each run was determined by triplicate titration of weighed aliquots of each solution with standardized 1 *N* NaOH solution. The H_0 value of each solution could then be read from a plot of H_0 *vs.* wt % H_2SO_4 for the solvent system used.[36]

Dehydrations of 1-aryl-2-phenylethanols in 60:40 dioxane–water plus $HClO_4$[46] were necessary because of the decreased solubility of multiply substituted *trans*-stilbenes. Kinetic solutions were made up so that a 3:2 volume (and hence, molar) ratio of dioxane and water is maintained at all acidities. Thus, use of standardized $HClO_4$ solutions, and the $HClO_4$ solution density data of Markham[47] was necessary. Kinetic experiments were carried out at 25.00 ± 0.02° as described in the previous section, and pseudo-first-order rate constants were calculated by the method described above. The acidity of each run (moles/liter of $HClO_4$) was determined by triplicate titrations of aliquots of known volume of each kinetic solution with standardized 1 *N* NaOH solution. The H_0 value of each solution could then be read from a plot of H_0 *vs.* molarity of $HClO_4$ for the solvent system used.[46,48]

Dehydration of 1-(2,4,6-Trimethoxyphenyl)-2-phenylethanol in "60% Dioxane." Into a 125-ml erlenmeyer flask was weighed 21.4878 g (0.1666 mol) of dichloroacetic acid (Matheson). The flask was swirled in an ice bath, and 73.12 ml of 1.1392 *N* NaOH solution was added from a buret. The resulting solution was warmed to room temperature and transferred to a 100.0-ml volumetric flask. The erlenmeyer was rinsed several times with small distilled water portions which were also transferred to the volumetric flask. The contents of the flask were diluted to the mark with distilled water to yield a solution effectively 0.833 *M* in both sodium dichloroacetate and dichloroacetic acid.

Kinetic solutions were formed in "60% dioxane" employing various concentrations of sodium dichloroacetate and dichloroacetic acid in a 1:1 molar ratio (hereafter referred to as DCA^-–HDCA), plus enough sodium perchlorate to make the ionic strength 0.300 *M*. To a given weighed amount of a DCA^-–HDCA solution were added, first, the appropriate amount of sodium perchlorate, and then, 14.90 ml of anhydrous, purified[49] dioxane. The kinetic experiment was begun by adding 0.10 ml of a dioxane stock solution of the appropriate strength to the volumetric flask and diluting to 25 ml with distilled water. The appearance of product was followed spectrophotometrically at 335 mμ in 1.00-cm quartz uv cells utilizing a Gilford Model 2000 recording spectrophotometer with a cell block thermostated at 25.00 ± 0.02°. By taking one point every 15 min, a photochemical *trans* to *cis* isomerization of the *trans*-2,4,6-trimethoxystilbene product, which occurred if the kinetic solution was monitored continuously, could be avoided. Control experiments using solutions of *trans*-2,4,6-trimethoxystilbene were employed to demonstrate the absence of photochemical isomerization quantitatively. An additional complication was that the dehydration reaction reached 94 ± 4% completion, after which the absorbance due to *trans*-2,4,6-trimethoxystilbene began to decrease very slowly. This anomaly could be shown to be due to an acid-catalyzed dimerization of the product stilbene which occurred even at spectrophotometric concentrations. This complication, however, rendered it impossible to obtain meaningful infinity points. Therefore, pseudo-first-order rate constants were obtained by submitting data from the first 80% reaction to computation by computer[50] under the nonlinear least-squares program LSKIN1,[50b] which calculates best values of the absorbance at zero time, the absorbance at infinite time, and the rate constant. At least 50 points at approximately equal time intervals were used in each calculation. This procedure sufficed to define the rate constant within usually 1%, and not more than 2%, standard deviation. An examination of the values of residuals, $A_{calcd} - A_{obsd}$, showed that they were completely random over the entire range of time used in the computation.

The molarity of each kinetic solution DCA^-–HDCA was predetermined by the method of forming solutions. Dichloroacetic acid–sodium dichloroacetate is not an effective buffer in purely aqueous solution. It may be shown,[51] however, that a constant pH meter reading for various concentrations of a 1:1 DCA^-–HDCA mixture in a mixed solvent is a necessary and sufficient condition to insure buffer characteristics of such a salt–acid com-

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Table I. Rate of Dehydration of 1-Aryl-2-phenylethanols at 25.00 ± 0.02°

A. In "5% Ethanol"–H_2SO_4

Compound	H_2SO_4, wt %	$-H_0$[b]	10^4k, sec^{-1}	$-\log k$
1-(4-Fluorophenyl)-2-phenylethanol[a]	49.34	3.33	1.18	3.93
	51.02	3.51	1.97	3.70
	53.04	3.73	3.83	3.42
	53.77	3.81	5.25	3.28
	56.74	4.16	15.9	2.80
1-(2-Methoxyphenyl)-2-phenylethanol	36.78	2.14	1.60	3.80
	38.67	2.29	2.55	3.59
	44.82	2.86	12.2	2.91
	48.33	3.23	39.3	2.40
1-(2-Methylphenyl)-2-phenylethanol	46.88	3.07	1.12	2.95
	49.27	3.32	2.40	3.62
	51.51	3.56	5.09	3.29
	54.68	3.92	13.1	2.88
1-(2-Fluorophenyl)-2-phenylethanol	57.25	4.22	0.732	4.14
	59.62	4.52	2.25	3.65
	61.61	4.76	7.14	3.15
	62.41	4.87	8.13	3.09
	63.26	4.99	17.6	2.75

B. In 60:40 (v/v) Dioxane–Water + $HClO_4$

Compound	$HClO_4$, M	$-H_0$[c]	10^4k, sec^{-1}	$-\log k$
1-(2,4-Dimethoxyphenyl)-2-phenylethanol	0.582	−1.28	1.02	3.99
	0.794	−0.98	2.31	3.64
	0.867	−0.88	3.16	3.50
	1.086	−0.61	5.98	3.22
	1.180	−0.51	8.15	3.09
1-(4-Methoxyphenyl)-2-phenylethanol	1.686	−0.04	0.47	4.33
	1.981	0.24	1.04	3.98
	2.376	0.58	2.99	3.52
	2.561	0.76	4.96	3.30
	2.767	0.94	8.76	3.06
1-(4-Methylphenyl)-2-phenylethanol	2.949	1.06	0.201	4.70
	3.261	1.30	0.424	4.37
	3.455	1.44	1.03	3.99
	3.662	1.60	1.52	3.82
	3.962	1.80	3.40	3.47
	3.963	1.81	3.55	3.45

[a] The rate of dehydration of the 4-fluoro analog was measured in order to ascertain that the fluoro substituent followed the σ^+ correlation defined by other substituents. [b] From ref 36. [c] From ref 46.

bination. Accordingly, a Corning Model 12 pH meter, equipped with a Beckman glass electrode, Model 40495, and a standard calomel electrode was first standardized in aqueous 0.1000 M potassium acid phthalate solution, then allowed to equilibrate in "60% dioxane" solution 0.300 M in sodium perchlorate. pH meter readings on each kinetic solution were taken, and the pH was shown to be constant at 3.02 ± 0.04, with deviations not showing any recognizable trend with changes of buffer concentration. The method of Van Uitert and Haas[52] was used to compute an approximate value for the dissociation constant of dichloroacetic acid in "60% dioxane" at an ionic strength of 0.300 M. The resulting pK_a, 3.2, confirms that 1:1 DCA$^-$–HDCA should be an effective buffer over the concentrations used. DCA$^-$–HDCA mixtures were used in 70% dioxane without a consideration of the pH problems by deWolfe and Roberts.[53] Despite the absence of conventional NBS pH meter standards for dioxane–water solutions (such standards are desirable in view of the great utility of dioxane–water solutions), use of the pH meter in buffer catalysis problems in dioxane–water solution appears to be an accepted technique.[53,54]

Isolation of Reaction Products. Into a 500-ml erlenmeyer flask were placed 236 ml of water, 4 ml of concentrated H_2SO_4, and 50 ml of 95% ethanol. 1-(2,4,6-Trimethoxyphenyl)-2-phenylethanol (700 ml) was dissolved in 10 ml of 95% ethanol and added to the above solution at room temperature; the mixture turned milky immediately. After the solution has been stirred 2 hr (in the dark), a white precipitate was noted in the reaction vessel. The precipitate was filtered, and the filtrate was neutralized with Na_2CO_3 and stirred overnight. More precipitate could be collected from this material; the total yield of solid was *ca.* 400 mg. *trans*-2,4,6-Trimethoxystilbene, identified by analysis, melting point, and spectra, was isolated by short-path distillation at 110° (10^{-5} mm). The residue which remained from the sublimation could be recrystallized from dioxane-water or chromatographed to yield a white solid, mp 192–193° identified by analysis, uv, ir, nmr, and mass spectra to be a dimer of 2,4,6-trimethoxystilbene, 1,3-bis(2′,4′,6′-trimethoxyphenyl)-2-phenyltetralin. It could be shown quantitatively that a reaction leading to much smaller amounts of this dimer at spectrophotometric concentrations was responsible for the anomalous kinetics reported above.

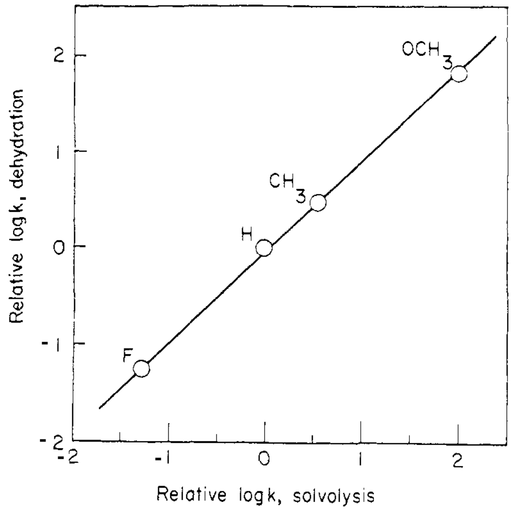

Figure 1. Correlation of the rates of dehydration of *ortho*-substituted 1-aryl-2-phenylethanols in "5% ethanol"–aqueous H_2SO_4 at 25° with rates of solvolysis of *ortho*-substituted *t*-cumyl chlorides in 90% aqueous acetone at 25°.

Noyce, Hartter, and Pollack[36] have shown that monosubstituted or unsubstituted 1-aryl-2-phenylethanols are quantitatively converted to the corresponding *trans*-stilbenes at spectrophotometric concentrations. No indication to the contrary was found in the remainder of this work. Infinity spectra were stable for five to ten half-lives, and were in complete agreement with those anticipated for the assumed reaction products.

Results and Discussion

The acidity dependence of the dehydration rates for the compounds studied is presented in Table I. Just as the rates of dehydration of *meta*- and *para*-substituted 1-aryl-2-phenylethanols (at $H_0 = -4.00$) correlated well with σ^+ [42] the rates (at $H_0 = -4.00$) of the *ortho*-substituted analogs correlate nicely with the rates of solvolysis of *ortho*-substituted *t*-cumyl chlorides[55] (the σ^+ defining reaction). This correlation is depicted in Figure 1. The slope of the correlation line, 1.1, is essentially equal to the ratio of ρ values for the two reactions defined by the σ^+ correlations for *meta* and *para* substituents.

If a ρ value is defined at $H_0 = 0$ for the dehydration in 60:40 (v/v) dioxane-water by a σ^+ correlation of the rates for the *p*-methoxy and *p*-methyl analogs, the values obtained is $\rho = -3.92$, a number which compares favorably with the value of −3.77 found in "5% eth-

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(52) L. G. Van Uitert and C. G. Haas, *J. Amer. Chem. Soc.*, **75**, 451 (1953).

(53) R. H. DeWolfe and R. M. Roberts, *ibid.*, **76**, 4379 (1954).

(54) T. H. Fife and L. K. Jao, *ibid.*, **90**, 4081 (1968).

(55) (a) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Amer. Chem. Soc.*, **79**, 1897 (1957); (b) H. C. Brown, Y. Okamoto, and G. Ham, *ibid.*, **79**, 1906 (1957); (c) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957).

Table II. Dehydration of 2,4,6-Trimethoxyphenylbenzyl Carbinol in "60% Dioxane" with 1:1 Sodium Dichloroacetate–Dichloroacetic Acid Mixtures at 25.00 ± 0.02°

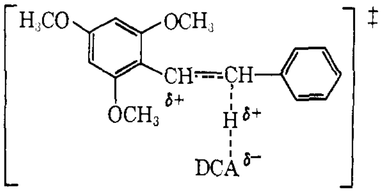
[HDCA],[a] M	[NaClO$_4$], M	$k \times 10^{-5}$ sec^{-1}
0.098	0.202	2.98 ± 0.03
0.129	0.171	3.24 ± 0.04
0.167	0.133	3.40 ± 0.02
0.199	0.101	3.60 ± 0.03
0.224	0.076	3.63 ± 0.03
0.248	0.052	3.77 ± 0.04

[a] [HDCA] = [Na$^+$DCA$^-$].

anol" and which is consistent with the somewhat lower dielectric constant of the dioxane–water system. If the rate for the 2,4-dimethoxy analog is fitted to the line, an "effective σ^+" for the "2,4-dimethoxy substituent" may be calculated to be -1.14. Under the assumption of additivity of substituent effects subtraction of -0.78, the σ^+ value for the 4-methoxy substituent, yields σ^+ (*o*-methoxy) = -0.36, in excellent agreement with the value of -0.33 calculated from the dehydration rate of 1-(2-methoxyphenyl)-2-phenylethanol.

The results outlined in the previous two paragraphs show that the reaction of *ortho*-substituted analogs is undoubtedly proceeding by the same mechanism as the reaction of the *meta*- and *para*-substituted compounds, and that mechanistic conclusions derived for *ortho*-substituted compounds should be applicable to *meta*- and *para*-substituted compounds. Likewise, the change in solvent from "5% ethanol"–H$_2$SO$_4$ to 60:40 (v/v) dioxane–water + HClO$_4$ appears to result in no mechanistic alteration.

The dependence of the pseudo-first-order rate constant for dehydration of 1-(2,4,6-trimethoxyphenyl)-2-phenylethanol on the concentration of a 1:1 DCA$^-$–HDCA buffer in "60% dioxane" is presented in Table II. It is clear from the data that this reaction displays general catalysis. The least-squares slope of the k *vs.* [HDCA] correlation line, k_{HDCA}, is 5.035×10^{-5} M^{-1} sec^{-1}, standard deviation 0.003 M^{-1} sec^{-1}, correlation coefficient 0.991. The standard deviation of k derived from this least-squares calculation is 0.04×10^{-5} sec^{-1}. The intercept of the correlation line, extrapolated to [HDCA] = 0, is 2.54×10^{-5} sec^{-1}; when divided by the concentration of hydronium ion in a 0.300 M NaClO$_4$ solution in "60% dioxane," 10^{-3} M, this number yields the second-order rate constant $k_{\text{H}_3\text{O}^+} = 2.5 \times 10^{-2}$ M^{-1} sec^{-1}. It would be fallacious to attempt to calculate a meaningful Brønsted α from only the two points k_{HDCA} and $k_{\text{H}_3\text{O}^+}$; however, the curvature normally associated with Brønsted plots over large ranges of buffer pK[56,57] suggests that calculation of a Brønsted α for the reaction using the two points for water and dichloroacetate would yield a lower limit of the true Brønsted α at the pK of dichloroacetic acid. Using the appropriate statistical correction of 2 for dichloroacetate ion, this value is calculated to be $\alpha \geqslant 0.42$. Because α and β for a given reaction sum to unity by definition,[57] then the Brønsted β for the dehydration is $\leqslant 0.58$. Evidently, if the molecular interpretations of the Brønsted β[56–58] are correct, it can be said that the proton undergoing elimination is <58% transferred in the transition state of the rate-determining step for dehydration. This transition state is most simply depicted as shown.



Because the dehydration of 1,2-diphenylethanol is the microscopic reverse of the hydration of *trans*-stilbene, it follows that the hydration of *trans*-2,4,6-trimethoxystilbene is a general acid catalyzed reaction with a Brønsted $\alpha > 0.42$ and therefore proceeds *via* rate-determining protonation of the olefinic double bond. Likewise, it is reasonable to assume, by analogy, that the hydrations of other *trans*-stilbenes are general acid catalyzed reactions. Because the existing evidence favors identical mechanisms for protonation of isomeric *cis*- and *trans*-stilbenes,[35] we conclude that the hydration (isomerization) of *cis*-stilbenes proceeds *via* a direct, rate-determining proton transfer. The evidence does not require the intermediacy of a π complex.

Schubert, Lamm, and Keefe[33] have pointed out that general acid catalysis does not rule out certain π-complex mechanisms involving "encumbered" carbonium ions. These mechanisms are not, however, the simplest ones which fit the observed experimental facts, and they may be tentatively set aside in the absence of other data.

A number of investigators have performed experiments which have rather clearly defined the conditions under which π complexes are most likely to exist. Dewar and Fahey[59] showed that, in the addition of an electrophile E$^+$ to a carbon–carbon multiple bond to yield a new C–E single bond and carbonium ion, π complexes are most likely to occur (other factors being equal) when E$^+$ is such that C–E bond energy is relatively small. Thus, I$^+$ and Br$^+$ are considerably more likely to form π complexes than H$^+$. A consideration of a large body of data in the literature[59,60] has also shown that evidence for the intermediacy of π complexes in polar additions is greatest for olefins which form relatively unstable carbonium ions and for additions in relatively nonpolar solvents. Clearly, additions of protons to multiple bonds in highly aqueous solution to yield resonance-stabilized carbonium ions are not likely to proceed *via* π complexes; that π complexes are not intermediates in carbon–carbon multiple bond protonation reactions in highly aqueous solution appears to be a general conclusion.

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(60) Leading references in this area are: (a) R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **89**, 2780 (1967), and preceding papers; (b) G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954); (c) G. S. Hammond and C. Collins, *ibid.*, **82**, 4323 (1960); (d) H. C. Brown and J. J. Melchoire, *ibid.*, **87**, 5269 (1965); and papers preceding; (e) M. L. Poutsma, *ibid.*, **87**, 4285 (1965).