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Isotope Effects in the Acid-catalyzed Isomerization of Cinnamic Acids[1-3]

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The solvent isotope effect upon the rate of isomerization of *cis*-cinnamic acids is substantial. At 25° in 47% sulfuric acid k_{H_2O}/k_{D_2O} is 6 for the isomerization of *cis-p*-methoxycinnamic acid. The Gross–Butler equation is not followed when the deuterium content of the solvent is varied. A detailed mechanism for the isomerization of *cis*-cinnamic acids is presented, a mechanism involving direct proton addition to give a solvated carbonium ion. Since the reaction rate parallels H_0 with unit slope, the acidity function is not a useful criterion for rate-determining proton transfers.

Introduction

The present series of papers[4-7] has been concerned with delineating the sequence of events in the acid-catalyzed isomerization of *cis*-cinnamic acid. Evidence has been presented to show that β-phenyl-β-hydroxypropionic acid is an intermediate in the isomerization,[4] that the slow step in the process occurs prior to the formation of β-phenyl-β-hydroxypropionic acid,[4] that the transition state for the isomerization has a great deal of carbonium ion character[1] and that deuterium is introduced during the course of the isomerization.[1,4]

In the examination of the behavior of the β-aryl-β-hydroxypropionic acids, it was shown that they likewise gave results supporting a carbonium ion intermediate,[6] and it was concluded that the rate-controlling step in the dehydration was the loss of the proton from the α-carbon.[5,7]

In the present study we wish to report on the results of carrying out the isomerization of cinnamic acids in sulfuric acid-d_2–deuterium oxide, in order to test mechanisms in which the rate-determining step is the direct proton transfer to the olefinic carbon of the *cis*-cinnamic acid.

Experimental

Kinetic procedures have been described previously.[4] **Sulfuric acid-d_2** was prepared by distilling sulfur trioxide into D_2O (99.8%). Material of desired acid strength was prepared by dilution with D_2O. All solutions were prepared by weight and titrations were carried out on weighed samples.

Results

Isomerization of *cis*-Cinnamic Acid in Sulfuric Acid-d_2.—The isomerization of *cis*-cinnamic acid was measured at 45° over a range of acid concentration in sulfuric acid-d_2–deuterium oxide. The rate data are given in Table I.

The isomerization in the deuterium solvent is substantially slower than in the protium solvent. When comparison is made at the same weight percentages sulfuric acid, the ratio k_{H_2O}/k_{D_2O} is 2.15 at 63.36% acid and 2.46 at 71.33% acid. If the ratio k_{H_2O}/k_{D_2O} be compared at the same mole fraction of sulfuric acid in the solution, k_{H_2O}/k_{D_2O} is 3.66 at 0.257 mole fraction and 4.16 at 0.332 mole fraction.

TABLE I

RATE OF ISOMERIZATION OF *cis*-CINNAMIC ACID IN SULFURIC ACID-d_2 AT 45.00°

D_2SO_4, %	$N_{D_2SO_4}$	$k_1 \times 10^5$, sec.$^{-1}$
63.36	0.2571	3.36
65.76	.2776	6.08
65.83	.2782	5.89
71.33	.3324	25.7

Very recently, Bunton and Shiner[8] have discussed the primary isotope effect on proton transfer mechanisms. For a rate-determining proton transfer, the maximum primary isotope of about 6 must be modified by considering the secondary isotope effects on hydrogen bonding of the solvated proton ($H_4O_9^+$). Bunton and Shiner conclude that "3.6 is the maximum value of k_{H_2O}/k_{D_2O} to be expected for any slow proton transfer from a hydronium ion." These conclusions, applicable in dilute aqueous solution, are clearly not to be applied directly in fairly concentrated sulfuric acid, where the solvation of the proton is obviously different from that in dilute acid.

It appears from our data that the primary solvent isotope effect gradually increases as the sulfuric acid concentration increases. In a recent study by Kuivila and Nahabedian[9] on the solvent isotope effect in the proton deboronation of areneboronic acids, values of k_{H_2O}/k_{D_2O} gradually increasing with sulfuric acid percentage were also observed.

Isomerization of Substituted Cinnamic Acids in Sulfuric Acid-d_2.—Measurements were also made of the rate of isomerization of *cis-p*-methoxycinnamic acid (Table II) and of *cis-p*-chlorocinnamic acid (Table III) in sulfuric acid-d_2.

TABLE II

RATE OF ISOMERIZATION OF *cis-p*-METHOXYCINNAMIC ACID IN SULFURIC ACID-d_2

D_2SO_4, %	$N_{D_2SO_4}$	$k + 10^5$, sec.$^{-1}$	D_2SO_4, %	$N_{D_2SO_4}$	$k \times 10^5$, sec.$^{-1}$
$T = 25.00°$			$T = 45.00°$		
42.28	0.1278	4.63	37.83	0.1085	16.0
47.36	0.1526	12.7	46.10	0.1461	79.5

The rate data are presented at various weight percentages of sulfuric acid-d_2.

In order to make comparisons of the solvent isotope effect, there are several choices which might be considered: at the same acidity value ($H_0 = D_0$), at the same weight per cent., at the same mole fraction, etc. There are several reasons for pre-

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[1] Paper XVIII in the Series Carbonyl Reactions; previous paper, D. S. Noyce and H. S. Avarbock, *J. Am. Chem. Soc.*, **84**, 1644 (1962).

[2] Presented in part at the Eighth Conference on Organic Reaction Mechanisms, Princeton, N. J., September, 1960.

[3] Supported in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[4] D. S. Noyce, P. A. King, Fred B. Kirby and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1632 (1962).

[5] D. S. Noyce and C. A. Lane, *ibid.*, **84**, 1635 (1962).

[6] D. S. Noyce, P. A. King, C. A. Lane and W. L. Reed, *ibid.*, **84**, 1638 (1962).

[7] D. S. Noyce and C. A. Lane, *ibid.*, **84**, 1641 (1962).

[8] C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 3214 (1961).

[9] H. G. Kuivila and K. V. Nahabedian, *ibid.*, **83**, 2164 (1961).

Table III

Rate of Isomerization of *cis-p*-Chlorocinnamic Acid in Sulfuric Acid-d_2

D_2SO_4, %	$N_{D_2SO_4}$	$k \times 10^5$, sec.$^{-1}$
	$T = 45.00°$	
68.25	0.3007	6.10
72.20	0.3420	18.0
	$T = 90.0°$	
52.68	0.1822	17.5

ferring comparisons at the same molarity, or at the same mole fraction. In the first instance, Högfeldt and Bigeleisen have concluded that $H_0 = D_0$ at the same molarity,[10] and that the pK's of the indicators differ, rather than that the H_0 and D_0 values differ with the indicators being of the same basicity.[11,12] Furthermore, the molar volumes of water and sulfuric acid are practically identical with water-d_2 and sulfuric acid-d_2,[13] respectively. Noonan and La Mer[14] have suggested that comparisons be made on a mole fraction basis. As the molar volumes of H_2O and D_2O are nearly identical, this makes a mole fraction comparison equivalent to comparison on a molar basis. Furthermore, mole fraction has the advantages of simplicity in calculation.

The density of sulfuric acid-d_2 solutions has been reported[15] in graphical form, but not sufficiently detailed for use. We have thus reported our data on a weight per cent. basis, and have made further comparisons on a mole fraction basis. Interpolations, where necessary, have been made using the rate data obtained in aqueous sulfuric acid.

Table IV summarizes the observed kinetic isotope effects for the three *cis*-cinnamic acids studied.

Table IV

Solvent Kinetic Isotope Effects

Acid	Temp., °C.	Acid, %	(k_{H_2O}/k_{D_2O}), %^{a}	$(k_{H_2O}/k_{D_2O})_N{}^b$
p-Methoxy-cinnamic	25.00	42.28	3.26	5.05
	25.00	47.36	3.69	6.02
	45.00	37.83	3.06	4.23
	45.00	46.10	3.16	5.25
Cinnamic	45.00	63.36	2.15	3.66
	45.00	65.76	2.27	3.68
		65.83	2.39	3.80
		71.33	2.46	4.16
p-Chloro-cinnamic	45.00	68.25	2.26	3.84
	45.00	72.20	2.43	4.02
	90.00	52.68	1.64	2.55

^{a} Kinetic isotope effect compared at the same wt.% sulfuric acid. ^{b} Kinetic isotope effect compared at the same mole fraction of sulfuric acid.

It is to be noted that the kinetic isotope effect shows a very sharp drop at the higher temperatures. This is a great deal more than would be calculated on the basis of a simple model assuming the loss of a single stretching vibration. The greater complexities of the solvent changes, of course, preclude such a simple comparison. It is probable that the combination of the direct primary kinetic isotope effect and the associated secondary isotope effects from the medium is responsible for the sharp temperature dependence of k_{H_2O}/k_{D_2O}.

Furthermore, the data show a distinct progression with the isotope effect increasing at higher acidities *with a given compound*.

Finally, upon comparing the isotope effects at the same temperature and the same acidity for the set of compounds, it is seen that there is a trend in the magnitude of the isotope effect. The isotope effect is largest in the case of *cis-p*-methoxycinnamic acid, and smallest with *cis-p*-chlorocinnamic acid.

Variation of Rate with Solvent Deuterium Content.—In addition to the interpretation of its magnitude, the solvent isotope effect has been used as a criterion of mechanism in another fashion. It has been suggested that the progressive replacement of hydrogen in the solvent by deuterium may lead to either a linear or non-linear change in rate. The treatment of Gross, Steiner and Suess[16] and the further developments of Orr and Butler[17] and Nelson and Butler[18] have resulted in several applications of the Gross–Butler equation as a tool in attempting to elucidate detailed mechanisms of proton transfer processes. These applications have recently been reviewed by Purlee[19] and by Gold.[20] However, the significance of the results in extending our structural understanding of transition states for proton transfer mechanisms is now extremely dubious. Gold,[20] and Halevi, Long and Paul[21] have pointed out reasons for questioning the significance of Gross–Butler treatments.

In our studies we have measured the rates of isomerization of *cis-p*-methoxycinnamic acid at 25° in solvents of varying isotopic composition in order to have available as complete a body of information as possible for evaluating the mechanism of the *cis–trans* isomerization. The direct experimental data are given in Table V.

Table V

Isomerization of *cis-p*-Methoxycinnamic Acid in Sulfuric Acid of Varying Isotopic Composition at 25.00°

N_D	Wt. % acid in mixture	$k + 10^5$, sec.$^{-1}$
0.00	47.36	46.8^a
.478	47.23	36.0
.593	46.27	26.0
.763	47.95	25.9
.998	47.36	12.7

^{a} Interpolated from data in previous paper, ref. 1.

The data are compared at a common mole fraction of catalyzing acid in Table VI. Clearly, the rate variation as the deuterium content of the

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(10) E. Högfeldt and J. Bigeleisen, *J. Am. Chem. Soc.*, **82**, 15 (1960).

(11) W. M. Schubert and H. Burkett, *ibid.*, **78**, 64 (1956).

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(18) W. E. Nelson and J. A. V. Butler, *ibid.*, 957 (1938).

(19) E. L. Purlee, *J. Am. Chem. Soc.*, **81**, 263 (1959).

(20) V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960).

(21) E. A. Halevi, F. A. Long and M. A. Paul, *J. Am. Chem. Soc.*, **83**, 305 (1961).

TABLE VI

RATE RATIOS IN THE ISOMERIZATION OF *cis-p*-METHOXYCINNAMIC ACID IN MEDIA OF VARYING ISOTOPIC COMPOSITION

N_D[a]	$k \times 10^4$, sec.$^{-1}$[b]	Obsd. k_N/k_H	Calcd. k_N/k_H linear	Calcd. k_N/k_H Gross–Butler
0.00	7.40	1.00	1.00	1.00
0.477	4.60	0.645	0.602	0.92
.593	3.78	.541	.506	.84
.763	2.59	.348	.364	.67
.998	1.23	.166	.166	.166

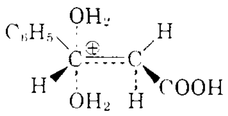
[a] Mole fraction total deuterium in solvent mixture. [b] Rate data interpolated to the common mole fraction of sulfate = 0.1520 from data in Tables II and V.

solvent is changed does not agree with the predicted values from the Gross–Butler treatment. Comparison with a linear interpolation between the rate in H_2O and the rate in D_2O is satisfactory.

Discussion

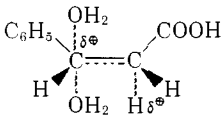
The large solvent isotope effect clearly indicates a direct proton transfer as the rate-determining process. This conclusion is further strengthened by conjoint consideration of the rate-determining process in the dehydration of β-phenyl-β-hydroxypropionic acid. In discussing the mechanism of the acid-catalyzed *cis–trans* isomerization and its relevance to other proton addition mechanisms, one of the most important facets of the cinnamic acid system is the nearly symmetrical nature of the reaction coördinate diagram proceeding from the hydroxy acid.

The data of Noyce and Lane[5,7] show clearly the mechanism of the dehydration of β-phenyl-β-hydroxypropionic acid to be a direct proton loss from the carbonium ion. Present day description of carbonium ions as symmetrically solvated species is quite well established, and we adopt this description here. Thus, the most adequate description of the final step in the dehydration sequence is *via* a transition state of structure C. In this transition state the proton being lost from the α-carbon has suffered some bond weakening as shown by the primary isotope effect[7] in this step, k_H/k_D = 2.77 at 45°. The carbonium ion character at the β-carbon is still high as shown by the large negative ρ-value of -4.6.



C

If the addition of a proton to *cis*-cinnamic acid be considered as the direct reverse of this process, arguments may be developed including the principle of microscopic reversability. True, the reaction is not carried out under equilibrium conditions; nevertheless, the close correspondence of the reaction pathways makes this approach a rational one. The primary difference is one of configuration, the cisoid or transoid arrangement of the carboxyl group and the aromatic ring. These considerations lead to a proposed detailed structure for the transition state of the addition of a proton to *cis*-cinnamic acid, formulated as D,



D

This transition state structure incorporates the following: the charge on the β-carbon is high, a conclusion supported by the large negative ρ in the isomerization reaction; the carbon–hydrogen bond at the α-carbon is partially formed, as supported by the kinetic isotope effects discussed.

This proposed description, moreover, accommodates many additional features of the data (though these by no means prove the specific structural arrangement D to be necessary or unique). The entropy of activation is in accord with this structure. The magnitude of the isotope effect at 25° in the case of *cis-p*-methoxycinnamic acid of k_H/k_D = 5–6 is accommodated; in addition to the factors discussed by Bunton and Shiner, the reduced nucleophilic nature of D_2O must be considered. Therefore, the proposed maximum rate factor k_H/k_D of 3.6 proposed by these authors would be increased. The parallelism with the encumbered carbonium ion suggested by Taft[22] in the isobutylene–*t*-butyl alcohol reaction is immediately apparent.

The Acidity Function and Rate-determining Proton Transfer.—It is abundantly clear from the previous discussion of mechanism that we have in hand a case of rate-determining proton transfer, and also that the acidity dependence of this mechanism follows the acidity function H_0 with almost exactly unit slope. Thus, the parallelism with the acidity function cannot be used as a criterion for or against a rate-determining proton transfer mechanism. This conclusion has been reached independently by several other investigators. Long and Paul[23] suggested that such might be the case in their review article. Melander and Myhre[24] pointed out the thermodynamic arguments concerning this point in considering aromatic exchange. More recently, Kresge and Chiang,[25] Long and Schulze[26] and Kuivila and Nahabedian[27] have observed that general acid catalysis, rate-determining proton transfer and the parallelism with the acidity function are observed in proton addition reactions on aromatic systems.

Taft has proposed that proton addition proceeds *via* a π-complex.[22,28] The evidence which we have accumulated does not show any necessity for a π-complex intermediate in the *cis–trans* isomerization. In fact, the present results argue against a π-complex, and show that the π-complex mechanism is not a general one.

On the other hand, the present results do not demonstrate that Taft is incorrect in his conclusions

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(22) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).

(23) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 835 (1957).

(24) L. Melander and P. C. Myhre, *Arkiv. Kemi*, **13**, 507 (1957).

(25) J. L. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **83**, 2877 (1961).

(26) F. A. Long and J. Schulze, *ibid.*, **83**, 3340 (1961).

(27) H. G. Kuivila and K. V. Nahabedian, *ibid.*, **83**, 2159 (1961).

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regarding the hydration of isobutylene. There are several kinds of information which are not parallel in the two systems. These are: the difference in the Gross–Butler correlation, the difference in entropies of activation, and the difference in the solvent isotope effect. It appears to the present authors that these differences may possible be explicable in terms of the differences in structure and stability of the reacting organic molecule and the resulting unstable intermediates, rather than in terms of different mechanisms. These points will need further study.

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Rate Data and Isomer Distribution in the Reactions of the Halobenzenes with Mercuric Acetate in Acetic Acid. Partial Rate Factors for the Mercuration Reaction[1—3]

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The rate constants and isomer distributions for the mercuration of fluorobenzene with mercuric acetate have been determined at 90, 70 and 50°. The product distribution at 90° is 59.4% *p*-, 6.9% *m*- and 33.7% *o*-; at 70°, 62.7% *p*-, 4.8% *m*- and 32.5% *o*-; at 50°, 66.7% *p*, 3.3% *m*- and 30.0% *o*-fluorophenylmercuric acetate, respectively. Utilizing earlier data for the mercuration of benzene under these conditions, the partial rate factors at 25° are calculated: p_f^F 2.98, m_f^F 0.040, o_f^F 0.63. These results indicate a small activation of the *para* position and a strong deactivation of the *meta* position. Because of the major side-reaction of mercuric acetate with the solvent, it was necessary to determine the reactivities of chlorobenzene and bromobenzene relative to benzene by a competitive procedure. At 90° the relative rates, $k_{ClC_6H_5}/k_{C_6H_6}$ and $k_{BrC_6H_5}/k_{C_6H_6}$ are 0.090 and 0.080, respectively. The isomer distribution for the mercuration of chlorobenzene at 90° is 48.4% *p*-, 21.5% *m*- and 30.1% *o*-; whereas bromobenzene yields 46.0% *p*-, 25.8% *m*- and 28.2% *o*-. The data were utilized to calculate the partial rate factors at 25°: chlorobenzene, p_f^{Cl} 0.36, m_f^{Cl} 0.060 and o_f^{Cl} 0.075; bromobenzene, p_f^{Br} 0.27, m_f^{Br} 0.054, o_f^{Br} 0.070. The results reveal a deactivation of all positions, least in the *para*. The order of reactivity in the *para* position is $F > H > Cl > Br$. In the *meta* position a different order is observed, $H > Cl \simeq Br > F$. The available data on the mercuration of monosubstituted benzene derivatives are assembled and examined. An excellent linear free energy correlation is obtained for the substitution data with the electrophilic substituent constants, σ^+, based on the solvolysis of the *t*-cumyl chlorides.

Introduction

The utility of the Selectivity Relationship[4] in correlating the available data for the substitution of aromatics has now been examined for a number of systems containing activating groups: toluene,[5] *t*-butylbenzene,[6] anisole,[7] biphenyl[8] and fluorene.[8]

Satisfactory correlations were achieved with toluene,[5f] *t*-butylbenzene[6d] and anisole.[7b] However, biphenyl exhibited a serious deviation.[8e] This deviation was attributed to a unique consequence of the biphenyl ring system. It was postulated that a steric energy barrier to coplanarity in the transition state was an important factor in the reactivity of biphenyl. It was argued that this energy barrier was, in part, overcome in electron-demanding reactions resulting in decreased and variable contributions by the *p*-phenyl substituent. In support of this interpretation, the limited data for the planar fluorene system appeared to give a reasonably good correlation with the Selectivity Relationship.[8e]

Alternative interpretations have been suggested. Thus the failure to achieve a satisfactory linear relationship with biphenyl has been attributed to the conflicting inductive and electromeric influences of the phenyl substituent.[9] Consequently, it appeared desirable to extend these investigations and to examine the substituent effects of groups exhibiting large electron-withdrawing inductive effects and equally important electromeric contributions. The halobenzenes are ideally suited for this purpose.

The results for the mercuration of the halobenzenes are summarized in the present paper. Data for the ethylation,[10a] acylation,[10b] and halogenation[10c] are presented in the following papers of this group. In the final paper,[10d] the applicability of the Selectivity Treatment to the available substitution data for the halobenzenes is examined.

Results

Fluorobenzene.—The rate of mercuration of fluorobenzene by mercuric acetate in glacial acetic acid was determined by following the decrease in mercuric acetate concentration titrimetrically with standard thiocyanate solution. A large excess of

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(1) Directive Effects in Aromatic Substitution. L.

(2) This research was supported by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

(3) Based upon a thesis submitted by Gordon Goldman in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(7) (a) H. C. Brown and M. Dubeck, *ibid.*, **82**, 1939 (1960); (b) L. M. Stock and H. C. Brown, *ibid.*, **82**, 1942 (1960).

(8) (a) H. C. Brown, M. Dubeck and G. Goldman, *ibid.*, **84**, 1229 (1962); (b) H. C. Brown and A. H. Neyens, *ibid.*, **84**, 1233 (1962); (c) H. C. Brown and G. Marino, *ibid.*, **84**, 1236 (1962); (d) H. C. Brown and L. M. Stock, *ibid.*, **84**, 1238 (1962); (e) L. M. Stock and H. C. Brown, *ibid.*, **84**, 1242 (1962).

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