Contributions of Steric, Electrical, and Polarizability Effects in Enantioselective Hydrolyses with *Rhizopus nigricans*: A Quantitative Analysis

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A quantitative analysis has been made of the contributions of steric, electrical, and polarizability effects to the enantiomeric excesses (ee) of alcohols formed in the hydrolysis of esters with the general formula ArCH(X)OAc by the mold *Rhizopus nigricans*. The results show that in this series the ee decreases with increasing size and electron-withdrawing ability of X and with increasing polarizability of Ar. A similar analysis was made for cyclic carbinols. The ability to delineate contributions made by conventional structure parameters in a reaction involving an intact microorganism now makes it possible to predict the optical purity as well as the absolute stereochemistry of an alcohol prepared by employing this microorganism.

Introduction

Hydrolytic enzymes have proven to be effective and practical reagents for the preparation of chiral acids.[1] The mechanism of the enzymic hydrolyses of the corresponding amides and esters and their stereoselectivities have been studied extensively.[2] Various models have been proposed to describe the interaction of the *acidic portion* of the substrate with the active site of the enzyme. However, the binding between the *alcohol portion* of an ester and the enzyme has received less attention. In an effort to develop a method for preparing chiral alcohols of a predictable configuration we found that a mold, *Rhizopus nigricans*, had an esterase, or family of esterases, which could be employed for the enantioselective hydrolysis of acetates.[3] Data on the absolute stereochemistry of the alcohol formed in this hydrolysis were used to formulate a rule (Figure 1) that analyzes the stereochemical course of a hydrolysis solely in terms of the relative sizes of substituents on the carbinol carbon. While the method has proven useful for the preparation of a variety of chiral alcohols, a qualitative description of the stereochemical course of the reaction entirely in terms of the "effective size" of substituents on the carbinol carbon ignored the possible roles of electrical and polarizability effects. In an attempt to assess their contributions we wanted to relate the enantiomeric excesses (ee) of the alcohols formed with these parameters. A better understanding of the factors that affect the relative hydrolyses rates of the two enantiomers would also be helpful in devising strategies for increasing the ee of the alcohols formed. Traditionally, the contributions that steric, electrical, and other parameters make to reaction rates have been determined from kinetic studies. While such studies are possible with purified enzyme preparations and with substrates where both enantiomers are available, our studies have employed racemic substrates and an intact microbe. As there are advantages in employing the entire microbe, we sought an alternative approach. A recent publication by Sih et al.[4] showed that in an analogous enzymic hydrolysis, information on percent conversion and the optical purity of the product formed was theoretically related to a parameter E, which reflects differences in the relative reaction rates of enantiomers (eq 1). Since we had collected data on hydrolyses mediated by *R. nigricans*, we have used that information to calculate E values for various substituents and have evaluated the relative importance of steric and electrical effects. Before describing that analysis, it is important to point out the limitations of the available data, which were collected in the course of establishing the synthetic utility of the microbial method. The method was intended to provide synthetically useful quantities of chiral compounds; therefore, hydrolyses were carried further toward completion than is desirable for calculating the most accurate E values. Furthermore, the estimates of the ee of the alcohols formed were based on optical rotation measurements, which are subject to significant errors. While cognizant of these limitations, we have nevertheless employed the available data in conjunction with the intermolecular force equation[5-7] shown below. The results of that analysis are gratifying, since they support an early assumption concerning the importance of steric factors while also providing an insight into the role of the polarizability of aromatic groups that was not apparent in earlier analyses. The quantitative analysis also explains at least one result that had been puzzling.

Calculations

Sih et al. have shown[4] that enzymically catalyzed kinetic resolutions can be described with a function E, the ratio of the kinetic parameters V_{max}/K, V_{max} being the maximum velocity for the two enantiomers and K, the Michaelis constant.

$$E = (V_A/K_A)/(V_B/K_B) \quad (1)$$

Applying their expressions to these hydrolyses, one obtains

$$E = \ln[1 - c(1 + \mathrm{ee(P)})]/\ln[1 - c(1 - \mathrm{ee(P)})] \quad (2)$$

where c, the precent hydrolysis, is represented by

$$c = 1 - (A + B)/(A_0 + B_0) \quad (3)$$

and A and A_0 are the final and initial concentrations of

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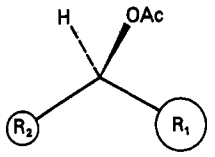


Figure 1. More rapidly hydrolyzed enantiomer $R_1 > R_2$.

Table I. Intermolecular Forces and Their Parameterization

intermolecular force	parameters
hydrogen bonding (hb)	n_H, n_n
dipole–dipole (dd)	σ_I
dipole–induced dipole (di)	σ_I, α
induced dipole–induced dipole (ii)	α
charge transfer (ct)	σ_I, σ_D
ion–dipole (Id)	i
ion–induced dipole (Ii)	i
steric effects on IMF	υ

parameter definitions

n_H = number of OH and/or NH bonds in the substituent
n_n = number of lone pairs on O and/or N atoms in the substituent
σ_I = localized (field and/or inductive) electrical effect parameter
σ_D = delocalized (resonance) electrical effect parameter
$\alpha = (MR_X - MR_H)/100$, where MR is the molar refractivity. It is a measure of the polarizability of the substituent.
1 = 1 for an ionic substituent and 0 for a nonionic substituent
$\upsilon = r_{VX} - r_{VH}$, where r_V is the van der Waals radius

the faster reacting enantiomer A. The final and initial concentrations of the slower reacting enantiomer are B and B_0. The enantiomeric excess (ee) of the product (P), is given by the expression

$$ee(P) = (P - Q)/(P + Q) \quad (4)$$

P is the concentration of the product derived from A, and Q is the concentration of the product derived from B.

The quantities V and K are related to structural effects by an intermolecular force (IMF) equation.[5] Thus, for a substrate bearing the substituent X, we may write

$$\log V_X = A_V\alpha_X + L_V\sigma_{IX} + H_{1V}n_{HX} + H_{2V}n_{nX} + I_Vi_X + S_V\upsilon_X + B_{0V} \quad (5)$$

The parameters and the intermolecular forces that they describe are defined and summarized in Table I. A similar equation can be written for K. Thus

$$\log K = A_K\alpha_X + L_K\sigma_{IX} + H_{2K}n_{nX} + I_Ki_X + S_K\upsilon_X + B_0 \quad (6)$$

Then

$$\log (V_A/K_A)_X = \log V_{AX} - \log K_{AX} \quad (7)$$

$$\log (V_A/K_A)_X = (A_V - A_K)\alpha_X + (L_V - L_K)\sigma_{IX} + (H_{1V} - H_{1K})n_{HX} + (H_{2V} - H_{2K})n_{nX} + (I_V - I_K)i_X + (S_V - S_K)\upsilon_X + (B_{0V} - B_{0K}) \quad (8)$$

An analogous relationship may be written for $\log (V_B/K_B)_X$. When the more reactive enantiomers all have the same absolute stereochemistry

$$\log E = (\log V_A - \log K_A) - (\log V_B - \log K_B) \quad (9)$$

$$\log E = A^*\alpha_X + L^*\sigma_{IX} + H^*_1n_{HX} + H^*_2n_{nX} + I^*i_X + S^*\upsilon_X + B^*_0 \quad (10)$$

where $A^* = A_{VA} - A_{KA} - A_{VB} + A_{KB}$ etc. It follows that the structural effects on the resolution of racemates by *R. nigricans* and presumably by other microorganisms should be quantitatively described by the IMF equation. The present study, to our knowledge, is the first test to determine whether a reaction catalyzed by an enzyme in an intact microorganism can be analyzed by using the IMF equation. Calculated values of E are listed in Table II, and the parameters used in the correlation are given in Table III.

Table II. Values of the Conversion, c, the Enantiomeric Enrichment of the Product, ee(P), and the Enantiomeric Ratio, E

A. Acyclic Acetates (1, 2)

ArCH(OAc)X					
Ar	X	c	ee(P)	E	calcd E
Ph	Me	0.45	0.79	16	10
Ph	CH_2Cl	0.16	0.52	3.5	5.4
Ph	C=CMe	0.59	0.51	6.5	4.2
Ph	Et	0.39	0.45	3.5	8.8
Ph	Pr	0.27	0.75	9.2	6.1
Ph	*i*-Pr	0.10	0.44	2.7	4.8
Ph	*t*-Bu	0.31	0.09	1.2	1.1
Ph	CF_3	0.23	0.08	1.2	1.3
Ph	CO_2Me	0.24	0.59	4.6	5.2
Ph	CH_2Ph	0.23	0.76	9.1	5.5
1-naphthyl	Me	0.33	0.995	320	99
2-naphthyl	Me	0.44	0.94	72	102
2-furyl	Me	0.44	0.22	1.8	5.9
2-thienyl	Me	0.64	0.36	3.9	5.7
2-pyridyl	Me	0.78	0.22	3.2	3.7
3-pyridyl	Me	0.53	0.83	37	3.9

B. Cyclic Acetates (3)

$C_6H_4CH(OAc)$-$CHZ(CH_2)_n$					
n	Z	c	ee(P)	E or E'	calcd E
1	H	0.53	0.42[b]	0.26[a]	
2	H	0.27	0.71	0.13[a]	
4	H	0.58	0.71	0.038[a]	
1	Me	0.44	0.38	2.9	2.9
1	Cl	0.29	0.40[b]	2.7	2.5
1	Br	0.35	0.71[b]	8.5	11
2	Me	0.42	0.22	1.8	1.5
2	Cl	0.19	0.18	1.5	1.3
2	Br	0.55	0.56	7.0	5.8

[a] E'. All other values are E. [b] The ee values differ from those previously reported. They have been corrected for a systematic error in the specific rotation of 1-indanol used in ref 3b.

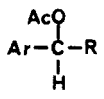
Table III. Parameter Values Used in the Correlations

X/Ar/Z	σ_I	α	υ
Me	−0.01	0.046	0.52
CH_2Cl	0.17	0.095	0.60
C=CMe	0.30	0.131	0.58
Et	−0.01	0.093	0.56
Pr	−0.01	0.139	0.68
i-Pr	0.01	0.140	0.76
t-Bu	−0.01	0.186	1.24
CF_3	0.40	0.040	0.90
CO_2Me	0.32	0.105	0.50
CH_2Ph	0.03	0.290	0.70
Ph	0.12	0.244	0.57
Br	0.47	0.079	0.65
Cl	0.47	0.050	0.55
1-naphthyl	0.14	0.406	0.57
2-naphthyl	0.13	0.406	0.57
2-furyl	0.17	0.169	0.57
2-thienyl	0.19	0.230	0.57
2-pyridyl	0.20	0.220	0.57
3-pyridyl	0.17	0.220	0.57

Results and Discussion

In analyzing the results for alkylarylcarbinols it was useful to treat separately the results for acyclic and cyclic esters. The acyclic esters were subdivided into two groups; the first is shown in structure 1 and the second group

corresponds to that shown as **2**. Values of E, calculated



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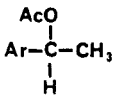

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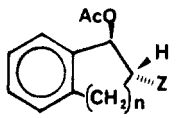

3

from the percent hydrolysis, c, and the ee of the product alcohols are listed in Table II.[3] Since none of the substituents in the series described by structure **1** is ionic, i.e., a hydroxyl or an amino group, the correlation equation becomes that shown as

$$\log E_X = A^*\alpha_X + L^*\sigma_{IX} + H^*_2 n_{nX} + S^*\upsilon_X + B_0 \quad (11)$$

The best equation obtained in a multiple linear regression analysis is

$$\log E_X = -1.20(\pm 0.417)\sigma_{IX} - 1.46(\pm 0.300)\upsilon_X + 1.85(\pm 0.243) \quad (12)$$

$$100R^2 = 82.07 \quad F = 13.73 \quad s = 0.192$$
$$s^0 = 0.519 \quad n = 9 \quad r_{\sigma\upsilon} = 0.207$$

where $100R^2$ is the percent of the variance of the data accounted for by the correlation equation. It is a measure of the goodness of fit; for example, when $100R^2 = 100$, the fit is perfect. F is a statistic that represents the significance for the coefficients of the correlation equation (often referred to as the regression coefficients). The larger the value of F, the better the fit. The standard error of the estimate is s. As values of s obtained under different experimental conditions are generally not comparable, comparisons are made by using s^0, which is the standard error of the estimate divided by the root mean square of the data. The smaller the value of s^0, the better the fit. The statistics r_{ab} are called zeroth-order partial correlation coefficients which describe the correlation of the parameter a with the parameter b. They constitute a test of the degree of colinearity of the two parameters. Even when two parameters are in principle independent of each other, they can be colinear within a given data set. The greater the degree of parameter colinearity, the more difficult it is to interpret the correlation equation. The smaller the value of r_{ab}, the greater is the independence of the parameters. In the above equation the coefficients for the polarizability (A^*) and the hydrogen-bonding (H_2) term are not significantly different from zero. Thus, the substituents exert steric and localized electrical effects. Other effects, if present, appear to cancel.

In analyzing the data for those compounds described by structure **2**, we have assumed that the appropriate steric parameter for the aromatic ring is its half-thickness. As this value is about the same for all the aryl groups studied, the steric effect is constant within the set. All the set members have the same absolute stereochemistry for the more rapidly hydrolyzed enantiomer, and the correlation equation is

$$\log E_{Ar} = A^*\alpha_{Ar} + L^*\sigma_{IAr} + H_2 n_{nAr} + B^*_0 \quad (13)$$

The best equation obtained is

$$\log E_{Ar} = 7.40(\pm 1.95)\alpha_{Ar} - 0.790(\pm 0.556) \quad (14)$$

$$100R^2 = 74.19 \quad F = 14.37 \quad s = 0.455$$
$$s_0 = 0.601 \quad n = 7$$

The polarizability of the aryl group has a large effect on the difference in reactivity of enantiomers in the series corresponding to **1** and **2**. Data on both series (**1** and **2**) have been combined into a single data set. The best equation is

$$\log E_{XAr} = -1.01(\pm 0.624)\sigma_{IX} - 1.33(\pm 0.449)\upsilon_X + 7.37(\pm 1.43)\alpha_{Ar} - 0.0961(\pm 0.502) \quad (15)$$

$$100R^2 = 80.70 \quad F = 15.34 \quad s = 0.336$$
$$s^0 = 0.513 \quad r_{\sigma\upsilon} = 0.096 \quad r_{\sigma\alpha} = 0.124 \quad r_{\upsilon\alpha} = 0.124$$

The alcohols obtained from the series described by **3** all have the same configurations. However, the configuration of the alcohol where Z = H is *different*. In order to include all the compounds in the same data set it is necessary to use the reciprocal of E_H or E'_H. As there are no ionic or hydrogen-bonding substituents (Z) in this set i, n_H, and n_n need not be considered as variables. The steric effect of the Me, Cl, and Br substituents is about the same (υ = 0.52, 0.55, and 0.65, respectively), while that for H is zero. The steric effect can therefore be represented by the parameter n_Z, which takes the value zero when Z is H and one when Z is Me, Cl, or Br. Only a polarizability effect is involved in varying the size of the ring in this series. We have assumed that the steric effect resulting from a change in ring size is negligible. The polarizability of the alkyl group is a linear function of the number of carbon atoms in the alkyl group.[8] The ring size has therefore been parameterized by n, the number of methylene groups in the ring. Then the correlation equation is

$$\log E\#_{Zn} = A^*\alpha_Z + L^*\sigma_{1Z} + B^*_1 n_z + B^*_2 n + B^*_0 \quad (16)$$

The best equation obtained is

$$\log E\#_{Zn} = 23.0(\pm 1.33)\alpha_Z - 0.341(\pm 0.161)\sigma_{IZ} - 0.261(\pm 0.0296)n - 0.338(\pm 0.0781) \quad (17)$$

$$100R^2 = 99.47 \quad F = 310.6 \quad s = 0.0746$$
$$s^0 = 0.0980 \quad n = 9 \quad r_{\alpha\sigma} = 0.755 \quad r_{\alpha n} = 0.393$$
$$r_{\sigma n} = 0.266$$

The excellent fit obtained is probably fortuitous.

In order to identify the contributions various effects make to the experimental E values, we have calculated E values for different substituents using eq 15 and 17 and have listed these in Table II. The calculation shows that the largest contribution made to the E value comes from the steric parameter for the group of compounds given by structures **1** and **2**. The observed variations in E are accounted for by the steric parameter and the polarizability of the substituents. The corrections attributed to electrical effects are quite small. The optical purity of the alcohol obtained from the hydrolysis of trifluoromethylphenylcarbinyl acetate was much less than expected.[3] In an effort to rationalize this observation we suggested that a special electrical effect was associated with a trifluoromethyl group. Our expectation of a larger ee was based on the assumption that trifluoromethyl and methyl groups are similar in size. However, υ, the steric parameter for the trifluoromethyl group, is intermediate in size between a methyl and a *tert*-butyl group.[9] When calculated and observed E values for this compound are compared, the difference in these values is found to be less than that observed for many other compounds. Hence the postulate of a special effect for the trifluoromethyl group is unnecessary.

As the experimental data employed in calculating E values have large errors, the observed agreement for many substituents is probably as good as one could expect. We

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(9) The values for methyl, trifluoromethyl, and *tert*-butyl are 0.56, 0.90, and 1.24, respectively.

therefore did not examine the abilities of other steric parameters to give a better correlation between calculated and observed E values.

The present analysis shows that some consideration of both the polarizability and the size of aromatic groups is required to account for the observed E values. This conclusion is consistent with findings made with other hydrolytic enzymes,[2] e.g., α-chymotrypsin, which exhibit esterase activity. The latter enzyme has been shown to contain a hydrophobic pocket that binds to aromatic groups and to large aliphatic groups, i.e., polarizable groups.

A smaller range in E values is observed in the group of carbinols described by structure **3** than in the acyclic series. As mentioned above, the steric effects of substituents at C-2 in this group were assumed to be essentially constant. The observed variation was accounted for by the electrical parameter σ_1 and the polarizability correction associated with the number of methylene groups in the ring. Despite these simplifications, the calculated E values account for the observed differences in E values for the same substituents in the 2-substituted 1-indanols and 1-tetraols.

One of the purposes of this study was to determine whether the data collected on the hydrolysis of a number of esters could be used in conjunction with the IMF equation to separate contributions made by (a) steric effects and (b) electrical effects and the polarizability of substituents. The present results indicate that it is possible to do so, and therefore it is now also possible to predict the ee of previously unexamined esters in one of these series. Perhaps an ability to quantitatively predict the optical purities of the products of these hydrolyses in concert with an ability to predict their absolute stereochemistry will encourage others to use this microbe as a chiral reagent.

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Reaction of Chloride Ion with Thiiranium Ions Prepared by Two Different Methods[1]

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It has been found that the kinetically controlled product of the reaction of chloride ion with the thiiranium ion formed in the same solvent and at the same temperature by means of two different reactions is the one formed by attack at the least substituted carbon.

Thiiranium ions[2] play an important role in the chemistry of bivalent sulfur compounds. They are involved as intermediates in (i) the solvolysis of β-chloroalkyl aryl sulfides, (ii) the alkylation of thiiranes, and (iii) the addition of arene- and alkanesulfenyl halides to alkenes.[3] Reactions involving thiiranium ions as intermediates have also found synthetic utility. A number of workers[4] have demonstrated how a double bond can be functionalized in an anti stereospecific manner by means of reactions involving thiiranium ion intermediates.

Work from this laboratory has concentrated on elucidating the influence of several parameters on the mechanism of the addition of arenesulfenyl chlorides to alkenes.[5] From studies of the effect of alkene structure on the rates and products of addition, it was concluded that the first step of the addition is rate determining,[6] a fact that was later confirmed by the use of heavy atom kinetic isotope effects.[7] In the product-determining transition state, attack by chloride ion occurs at the least hindered carbon of the thiiranium ion.[8]

This last conclusion is in contrast to the reactions of stable thiiranium ions that are reported to undergo reactions with nucleophiles at the most substituted carbon.[9] While much has been made of this difference,[10] two facts must be pointed out. First, the two reactions occur under very different experimental conditions. Stable thiiranium ions are prepared in polar solvents such as liquid SO_2 at −70 to −30 °C while the addition reactions are usually

(1) Reactions of Sulfenyl Chlorides and their Derivatives. 25. Part 24: Schmid, G. H.; Garratt, D. G.; Dean, C. *Can. J. Chem.*, in press.

(2) The term thiiranium ion has been and is used to designate the positively charged three-membered sulfur-containing ring irrespective of the location of the counterion. This is analogous to the original practice of Winstein who referred to the carbocation portion of all ion pairs as varieties of carbonium ions. See: Winstein, S.; Klinedinst, P. E., Jr.; Robinson, G. C. *J. Am. Chem. Soc.* **1961**, *83*, 885.

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