# EMPIRICAL PARAMETERS OF ($E-Z$) ISOMERIZATION

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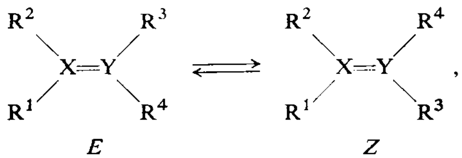
Equilibrium constants of ($E-Z$) isomerization of compounds A—CH=CH—B can be expressed, on the basis of factor analysis, in the form $\log K(Z/E)_{AB} = a_{A1}F_{1B} + a_{A2}F_{2B}$, where the first term corresponds to electrostatic interactions of substituents in the isomers and the second term expresses the difference in steric interactions.

For explanation of position of the ($E-Z$) equilibrium the substituent parameters $\lambda^d$ were suggested[1] which enable prediction of the equilibria of some olefins, enamines, Schiff's bases, hydrazones, and nitrones.
Supposing the general equation

$$\ln K(E/Z) = \varrho_{XY}[\lambda^d(R^1) - \lambda^d(R^2)]/[\lambda^d(R^3) - \lambda^d(R^4)] \qquad (1)$$

which relates to the reaction



(*A*)

where $\varrho_{XY}$ means the sensitivity factor, we can choose the origin for a standard substituent, *e.g.* $\lambda^d(H) = 0$, and fix the scale with the parameter $\lambda^d(CH_3) = 1$. This equation represents a linear free energy relationship (LFER) corresponding to the ($E-Z$) equilibria. Knorr interprets the $\lambda^d$ parameters predominantly as sterical ones, we tried to interpret them by means of regression analysis with other known parameters or with combination of other constants. Using the factor analysis, we tried to derive another possible relation for prediction of equilibria. The analysis was carried out for the olefins A—CH=CH—B, the equilibrium constants $K(Z/E)$ being taken from the least possible number of literature data to ensure homogeneity of data and to avoid systematical errors, and the constants chosen were those measured in media of lowest polarity and at close temperatures.

For the basic substituents on the double bond we chose $CH_3$, $C_2H_5$, $(CH_3)_2CH$, $(CH_3)_3C$, $C_6H_5$, Cl, OR, SR, CN, and COOR which exhibit various types of substituent effects. In the OR, SR, and COOR substituents we preferred $R = CH_3$ to eliminate conformational effects on the interpretation, but with respect to the above-mentioned reasons in selection for some compounds it was necessary to choose also alkyl groups with longer chains. The data were arranged in a table with 10 rows and 10 columns (Table I). The missing values (denoted by 0 at the respective position) for pure olefins and olefins with alkoxycarbonyl group were estimated from the $\lambda^d$ parameters using the equation $\ln K(E/Z) = 0{\cdot}95\lambda^d(R^2)\,\lambda^d(R^4)$. The sensitivity factor of this equation was calculated from the equilibrium of 2-butene[2], $R^2$, $R^4$ = = alkyl, COOR and $R^1$, $R^3$ = H. The other unknown values (empty frames in Table I) were supplied by another way.

First we examined the correlation of the $\lambda^d$ parameters with known sterical parameters. The correlation coefficient $r = 0{\cdot}65$ was found for the $A$ parameter[22] ($-\Delta G$ of the equilibria equatorial/axial substituent in cyclohexane) by linear regression for 12 values, the correlations being also bad for the Taft $E_S$ constants[23] or $E_S^0$ constants[24] and for $F^H$ constants[24], and even addition of the $\sigma_R^-$ constants to the $A$ constants in the stepwise regression procedure does not make the correlation much better (the total correlation coefficient $R = 0{\cdot}82$). Although sterical effects are significant, they only represent a part of the set of effects involved in the $\lambda^d$ parameter.

The equilibrium constants[5] for compounds X—CH=CH—$OC_2H_5$, X = Cl, $CH_3$, $C_2H_5$, $(CH_3)_2CH$, $(CH_3)_3C$, $C_6H_5$, $OC_2H_5$, and $CH=CH_2$, were treated by linear regression. For the correlation of the respective $\log K(Z/E)$ with the $A$ values we found $r = 0{\cdot}89$, hence in this series sterical effects represent the dominant component even though not the only one. The $A$ parameters are most useful for these correlations, being derived from the sterical interactions which exhibit model relation to interactions of the substituents on the double bond.

For treatment of the $\log K(E/Z)$ data by stepwise regression procedure we selected the $(E-Z)$ data sets from the equilibria of compounds $R^1$—CH=CH—X, where $R^1$ = $CH_3$, $C_2H_5$, Cl, CN, and COOR. The basic substituents X given in Table I were complemented (for $R^1$ = $CH_3$, $C_2H_5$, and Cl) by other ones for which the $\log K(Z/E)$ values are known (Table II).

Combinations of the $A$ parameters with $\sigma_P^0$, $\sigma_I + \sigma_R^0$, and $\sigma_R^-$ were chosen as independent variables for $R^1$ = $CH_3$, $C_2H_5$, and Cl. In the last combination mentioned the $\sigma_R^-$ constants were taken into account because of electron-donor character of $R^1$ and of the fact that $\sigma_R^-$ describes direct interaction in the conjugated system. In the first two combinations of independent variables, only the $A$ constants always entered the regression according to the $F$-values for input and involvement in the regression, the partial correlation coefficient $r < 0{\cdot}9$.

Both the constants were significant in the combination of $A$ and $\sigma_R^-$ for $R^1$ = $CH_3$ and $C_2H_5$, the total correlation coefficients are R = 0·89 and 0·94, the effect expressed

TABLE I

The log $K(Z/E)$ values of $(E-Z)$-isomerization of 1,2-substituted olefins $R^2—CH=CH—R^4$ (in brackets are given references)

| $R^4$ \ $R^2$ | Cl | $CH_3$ | $C_2H_5$ | $(CH_3)_2CH$ | $C_6H_5$ | $(CH_3)_3C$ | OR | SR | COOR | CN |
|---|---|---|---|---|---|---|---|---|---|---|
| Cl | (3) 0·217 | (4) 0·363 | (3) 0·272 | (3) −0·244 | (3) −0·588 | (3) −0·860 | (5)[a] 0·655 | (6) −0·252 | (7) −0·824 | (3) 0·188 |
| $CH_3$ | (4) 0·363 | (2) −0·420 | (2) −0·575 | (8) −0·638 | (9) −1·222 | (8) −3·097 | (5)[a] 0·141 | (11) 0·025 | (10) −0·796 | (12) 0·124 |
| $C_2H_5$ | (3) 0·272 | (2) −0·575 | (2) −0·788 | 0[b] −0·900 | (13) −1·061 | 0[b] −1·700 | (5)[a] −0·058 | (14) −0·123 | (10) −1·229 | (15) −0·004 |
| $(CH_3)_2CH$ | (3) −0·244 | (8) −0·638 | 0[b] −0·900 | 0[b] −1·030 | 0[b] −1·960 | 0[b] −1·960 | (5)[a] −0·234 | (16) −0·158 | (16) −4·000 | (17) −0·523 |
| $C_6H_5$ | (3) −0·588 | (9) −1·222 | (13) −1·061 | 0[b] −1·960 | (18) −4·000 | 0[b] −3·172 | (5)[a] −0·138 | | (7) −2·155 | (17) −0·602 |
| $(CH_3)_3C$ | (3) −0·860 | (8) −3·097 | 0[b] −1·700 | 0[b] −1·960 | 0[b] −3·172 | (19) −4·000 | (5)[a] −0·899 | | 0 −3·094 | (17) −2·000 |
| OR | (5)[a] 0·655 | (5)[a] 0·141 | (5)[a] −0·058 | (5)[a] −0·234 | (5)[a] −0·138 | (5)[a] −0·899 | (5)[a] 0·602 | (6)[a] −0·155 | (7) −2·041 | (3) −0·252 |
| SR | (6) −0·252 | (11) 0·025 | (14) −0·123 | (16) −0·158 | | | (6)[a] −0·155 | (3) −0·260 | (7) −1·222 | (3)[c] 0·053 |
| COOR | (7) −0·824 | (10) −0·796 | (10) −1·229 | (16) −4·000 | (7) −2·155 | 0[b] −3·094 | (7) −2·041 | (7) −1·222 | (20) −1·018 | (7) −0·921 |
| CN | (3) 0·188 | (12) 0·124 | (15) −0·004 | (17) −0·523 | (17) −0·602 | (17) −2·000 | (3) −0·252 | (3)[c] 0·053 | (7) 0·921 | (21) −0·284 |

[a] $R = C_2H_5$; [b] 0 is the value estimated from the $\lambda^d$ parameters; [c] $R = C_4H_9$.

by the $\sigma_I$ constant being less significant. For $R^1$ = COOR and CN the stepwise regression procedures were carried out with the $A$, $\sigma_P^0$, and $\sigma_R^+$ parameters network. In both the combinations the $A$ variable only entered the regression, $r < 0.8$. As the $\lambda^d$ substitution parameters are derived directly from experimental data and cannot be described by the parameters given, the correlations of $\log K(Z/E)$ with broader network of these parameters were unsuccessful.

With the aim of determination of additivity of sterical effects described by the $A$ parameter we examined a correlation of a set of 66 compounds A—CH=CH—B with the sum and the product of $A$ (the values given in Tables I, II, the values for combinations of halogens[28-29], the value[30] for A = B = $SC_6H_5$, and finally[31] that for A = $(CH_3)_2N$, B = $COOCH_3$): the product $A_A \cdot A_B$ appears to be a substantially better parameter for partial explanation of the ($E-Z$) equilibria of the compounds mentioned, thus the sterical effects represented by the $A$ values are not additive. Polynomial regression was also examined for the compound set given,

$$\log K(Z/E) = a + b(A_A \cdot A_B) + c(A_A \cdot A_B)^2 + d(A_A \cdot A_B)^3 ,$$

however, coefficients of the higher powers are close to zero, and the correlation coefficients of the quadratic and cubic regressions differ but slightly from the linear regression. Furthermore, we tried to describe the ($E-Z$) equilibria by means of the principal component analysis (PCA) and iterated principal factor analysis[32] (PFA).

The PCA and PFA models have the form given by Eqs (2) and (3), respectively.

$$Y_{ji} = \sum_{p=1}^{m} a_{jp} F_{pi} \qquad (2)$$

TABLE II

Further log $K(Z/E)$ values of the ($E-Z$)-isomerization of compounds $R^1$—CH=CH—X (in brackets are given references)

| $R^1$ \ X | F | Br | I | $COCH_3$ | $SO_2CH_3$ | $SOCH_3$ | $N(CH_3)_2$ | $NO_2$ |
|---|---|---|---|---|---|---|---|---|
| $CH_3$ | (4) 0·360 | (4) 0·384 | — | (25) −2·178 | (11) −2·370 | (11) −0·534 | (26) −1·310 | — |
| Cl | (27) 0·314 | — | — | (3) −1·456 | — | — | — | — |
| COOR | — | (7) −0·908 | (7) −0·989 | — | — | — | — | (7) −2·60 |

$$Y_{ji} = \sum_{p=1}^{m} a_{jp}F_{pi} + \alpha_j U_{ji} \qquad (3)$$

$Y_{ji}$ corresponds to $\log K(Z/E)$ expressed in standard score with unit dispersion variance of the $j$ variable in the case $i$.

$a_{jp}$ = loading of the $p$-th factor of the $j$ variable: it describes the effect of the $p$-th factor on the value of $\log K(Z/E)$,
$F_{pi}$ = value of the common $p$ factor in the case $i$ (factor score),
$U_{ji}$ = unique factor explaining the dispersion variance of the respective variable, $\alpha_j$ means its loading. The product $\alpha_j U_{ji}$ represents the residual error.

Both $a$ and $F$ were further treated as parameters describing the $(E-Z)$ equilibrium, $j = i$ = Cl, $CH_3$, $C_2H_5$, $(CH_3)_2CH$, $C_6H_5$, $(CH_3)_3C$, OR, SR, COOR, and CN.

If the Table I is taken as a data matrix $\mathbf{Y} = Y_{ji}$, the PCA and PFA models can be transcribed into matrix form as $\mathbf{Y} = \mathbf{AF}$ and $\mathbf{Y} = \mathbf{AF} + \mathbf{DU}$. Magnitude of the $\mathbf{Y}$ matrix is $10 \times 10$, that of $\mathbf{A}$ matrix (the factor model) is $10 \times m$, $\mathbf{D} = \text{diag}\,\{\alpha_1, \ldots \ldots, \alpha_n\}$, $\mathbf{F}$ matrix (matrix of the factor values) $m \times 10$, and the $\mathbf{U}$ matrix (the matrix of unique factors) $10 \times 10$.

The $\mathbf{A}$ matrix was assessed by iteration[33] in the form of the product $\mathbf{AA}'$ which approximates the reduced correlation matrix $\mathbf{T} = \mathbf{AA}'$ obtained by application of the matrix model to the matrix of selection correlations $\mathbf{R}^+ = \mathbf{YY}'/10$ with the presumption that the factors cannot be correlated. Calculation of $\mathbf{R}^+$ represents the beginning of the whole procedure, however $\mathbf{R}^+$ was not positively semidefinite, which means that one of criteria of the iteration cycle is not fulfilled. This property was regained by obtaining the reestimated correlation matrix $\mathbf{R}$ which, however, is not singular (rank $n = 8$) whereby all other methods are excluded except for PFA and PCA.

The missing values of the data matrix $\mathbf{Y}$ were estimated by the stepwise regression procedure. The $SMC_j$ (squared multiple correlation) of the variables with the factors were taken as the initial values of the communalities forming the diagonal of $\mathbf{T}$ matrix. In both the methods the solution was restricted to 2 factors, as it can be seen from the share of the individual factors in the whole variance explained (Table III), *i.e.*, the $\mathbf{A}$ matrix has the magnitude of $10 \times 2$, and the $\mathbf{AA}'$ matrix of magnitude $10 \times 10$ approximates $\mathbf{T} = \mathbf{R}$ and (only) $\mathbf{T}$ in PCA and PFA, respectively.

Rotations of matrix $\mathbf{A}$ to matrix $\mathbf{A}^*$ were carried out by iterative minimizing the simplicity criterion G (ref.[32]).

$$G = \sum_{p \neq q} \left[ \sum_j a_{jp}^2 a_{jq}^2 - \frac{\Gamma}{10} \left(\sum_j a_{jp}^2\right)\left(\sum_j a_{jq}^2\right) \right],$$

where $p, q = 1, 2$, and $a_{pq}$ is the matrix of factor loadings. The $\Gamma$ value is decisive for the rotation: $\Gamma = 1$ for orthogonal rotation (the varimax method) and $\Gamma = 0$ for oblique rotation. The convergency criterion chosen for the rotation was $10^{-5}$. The relation of matrix $\boldsymbol{A}$ to matrix $\boldsymbol{A}^*$ is given by the equation $\boldsymbol{A}^* = \boldsymbol{AP}$, where $\boldsymbol{P}$ is a matrix of $2 \times 2$ magnitude (a plane), for which it is $\boldsymbol{PP}' = \boldsymbol{I}$ and which is related to the minimum value of $G$.

Table IV gives the rotated factor models $\boldsymbol{A}^*$. The rotation increased the share of the second factor in the total variance explained, VP (Table III), *i.e.* its effect on the result of $(E-Z)$ isomerization is comparable with that of the first factor. On the whole, the factor loadings of the three procedures mutually correspond, which indicates that the solution has physical meaning. Estimate of the $\boldsymbol{F}$ matrix was carried out by multiplication of the standard score of original variables by coefficients of factor values. Table V gives the individual $F_{pi}$ elements already related to the original variables. From the correlation matrix of the factor values it follows, that the factors are, in fact, non-correlated ($r = 0{\cdot}25$), *i.e.* that the factor model $\boldsymbol{A}$ or $\boldsymbol{A}^*$ is identical with the factor structure, and the solution can be written in the form

$$\log K' = a_{A1}F_{1B} + a_{A2}F_{2B}\,, \qquad (4)$$

where $\log K'$ means the standard score of $\log K(Z/E)$, $F_{1B,2B}$ are the factor values, and $a_{A1,A2}$ are their loadings.

The $F_2$ factor values are correlable with the $A$ values for PCA – orthogonal rotation according to the equation $A = 7{\cdot}103 - 5{\cdot}812F_2$, $r = -0{\cdot}96$ and for PCA – oblique rotation according to the equation $A = 7{\cdot}079 - 5{\cdot}982F_2$, $r = -0{\cdot}98$; the correlation is worse ($r = -0{\cdot}84$) for PFA – oblique rotation.

TABLE III

Share of the individual factors in the total variance with respect to the $\boldsymbol{A}$ matrix

| Factor (m) | Variance explained | |
|---|---|---|
| | PCA | PFA |
| 1 | 6·157 | 6·012 |
| 2 | 2·369 | 2·225 |
| 3 | 0·751 | 0·316 |
| 4 | 0·333 | 0·181 |
| 5 | 0·210 | 0·076 |
| 6 | 0·123 | −0·007 |
| 7 | 0·039 | −0·034 |
| 8 | 0·017 | −0·112 |
| 9 | 0·000 | −0·152 |
| 10 | 0·000 | −0·268 |

TABLE IV
The rotated factor models **A***

| $j$ | PCA $\Gamma = 1$ Factor 1 | PCA $\Gamma = 1$ Factor 2 | PCA $\Gamma = 0$ Factor 1 | PCA $\Gamma = 0$ Factor 2 | PFA $\Gamma = 0$ Factor 1 | PFA $\Gamma = 0$ Factor 2 |
|---|---|---|---|---|---|---|
| Cl | 0·764 | 0·536 | 0·751 | 0·446 | 0·645 | 0·506 |
| $CH_3$ | 0·370 | 0·893 | 0·265 | 0·865 | 0·175 | 0·919 |
| $C_2H_5$ | 0·609 | 0·733 | 0·531 | 0·668 | 0·458 | 0·720 |
| $(CH_3)_2CH$ | 0·952 | 0·188 | 0·952 | 0·064 | 0·924 | 0·137 |
| $C_6H_5$ | 0·526 | 0·754 | 0·444 | 0·701 | 0·369 | 0·731 |
| $(CH_3)_3C$ | 0·600 | 0·654 | 0·532 | 0·588 | 0·444 | 0·634 |
| OR | 0·941 | 0·150 | 0·946 | 0·026 | 0·899 | 0·109 |
| SR | 0·951 | −0·168 | 0·997 | −0·301 | 1·008 | −0·242 |
| COOR | 0·008 | 0·705 | −0·82 | 0·721 | −0·060 | 0·593 |
| CN | −0·292 | 0·903 | −0·415 | 0·956 | −0·479 | 0·942 |
| VP | 4·510 | 4·016 | 4·319 | 3·776 | 3·898 | 3·881 |

TABLE V
The factor values for the original variables

| $i$ | PCA $\Gamma = 1$ Factor 1 | PCA $\Gamma = 1$ Factor 2 | PCA $\Gamma = 0$ Factor 1 | PCA $\Gamma = 0$ Factor 2 | PFA $\Gamma = 0$ Factor 1 | PFA $\Gamma = 0$ Factor 2 |
|---|---|---|---|---|---|---|
| Cl | 0·713 | 0·835 | 0·817 | 0·917 | 0·769 | 0·682 |
| $CH_3$ | 0·392 | 0·209 | 0·416 | 0·256 | 0·322 | 1·017 |
| $C_2H_5$ | 0·233 | 0·198 | 0·257 | 0·225 | 0·453 | −0·928 |
| $(CH_3)_2CH$ | 0·173 | −0·607 | 0·092 | −0·581 | 0·029 | −0·155 |
| $C_6H_5$ | −0·334 | −0·861 | −0·445 | −0·896 | −0·435 | −0·715 |
| $(CH_3)_3C$ | −0·264 | −2·273 | −0·560 | −2·888 | −0·326 | −2·733 |
| OR | 1·115 | 0·453 | 1·165 | 0·587 | 0·918 | 1·277 |
| SR | 0·212 | 0·451 | 0·270 | 0·474 | 0·479 | 0·396 |
| COOR | −0·576 | 0·916 | −2·433 | 0·592 | −2·490 | 0·274 |
| CN | 0·337 | 0·783 | 0·437 | 0·819 | 0·451 | 0·739 |

The second factor corresponds to energy difference of steric interactions of the two isomers which can be modelled by means of $A$. The $F_1$ factor is probably related to the difference of electrostatic forces between the substituents in the ($E$) and ($Z$) isomers which represents a residual effect which remained unexplained besides the steric effect. If the loadings of the first factor are correlated with the $\sigma_R^-$ constants, the $r$ values reach up to $-0{\cdot}85$ to $-0{\cdot}88$; this expresses an influence of electrostatic induction on conjugation ability of the system (in terms of deviation from the charge distribution in the standard compound). In cases of compounds with distinct predominance of ($E$) isomers, *i.e.* those containing substituents as $(CH_3)_2CH$, $(CH_3)_3C$, and $C_6H_5$, the main reason for the position of the equilibrium lies in the steric effect. In the case of COOR substituent (with respect to its relatively low $F_2$ and the $A$ value correlable therewith) the main reason for usual predominance of $E$-isomers lies in other interactions (the residual effect), *e.g.*, of electrostatic nature which even can result in predominance of Z-isomer in the case of NC—CH=CH—CN. A more precise physical meaning of the two factors can be followed by construction of suitable models or by quantum-chemical methods.

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