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Robert E. Gawley. Do the Terms "%ee" and "% de" Make Sense as Expressions of Stereoisomer Composition or Stereoselectivity?

Page 2414. The following clarification is offered to avoid incorrect calculations of the selectivity factor in kinetic resolutions. The terms S_R and S_S in eq 9 were inadvertently defined differently from the same terms in eqs 11−13. The formula for calculating the selectivity factor in a kinetic resolution may therefore be misinterpreted, causing errors in calculations of **s**. Regarding eq 9, it must be recalled from eq 5 that $S_R + S_S = 1 - C$.

$$S_R + S_S + C = 1 \tag{5}$$

$$\mathbf{s} = \frac{\ln(S_R - S_S - C + 1)}{\ln(S_S - S_R - C + 1)} \tag{9}$$

Therefore, the S_R and S_S terms in eq 9 are not the fractions obtained by normalizing enantiomer ratios. If one wishes to use the normalized enantiomer ratio, in which the fractions of each enantiomer, *R* and *S,* add to 1 (e.g., 0.83 + 0.17, obtained from a normalized er of 83:17), the er fractions should each be multiplied by the quantity (1 − C) to obtain the correct S_R and S_S terms for eq 9.

An example illustrates the correct calculation. Assume that the percent conversion is 45% (C = 0.45), and the *S/R* er normalized as a percent is 83:17. The fraction of original substrate remaining (1 − C), is 0.55, and the calculation of **s** using eq 9 is as follows:

$$\mathbf{s} = \frac{\ln[(0.55)(0.17) - (0.55)(0.83) - 0.45 + 1)]}{\ln[(0.55)(0.83) - (0.55)(0.17) - 0.45 + 1)]} = \frac{\ln[0.187]}{\ln[0.913]} = 18.4$$

An alternate expression for calculating **s**, using the er fractions *R* and *S* for unreacted substrate (see also eq 1), is eq 9a.

$$\mathbf{s} = \frac{\ln[(1 - C)(R - S + 1)]}{\ln[(1 - C)(S - R + 1)]} \tag{9a}$$

The terms S_R and S_S in eqs 11−13 and the *y* (ordinate) axis in Figure 3, *are* the normalized enantiomer fractions of substrate, equivalent to *R* and *S* in eqs 1 and 9a.

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