LETTER TO THE EDITOR

Competitive Hydrogenation Rates of Monoenes

Sir: The relative hydrogenation rates of isomeric monoenes can be determined under competitive conditions using a recently developed technique (C.R. Scholfield, T.L. Mounts, R.O. Butterfield and H.J. Dutton, JAOCS 48:237 [1971]; T.L. Mounts, R.O. Butterfield, C.R. Scholfield and H.J. Dutton, JAOCS 47:79 [1970]; however many workers may not be prepared to undertake the complex mathematical analysis reported in these publications. I wish to show that for the simplest and probably most usual case, the analysis reported is neither necessary nor particularly efficient, and to suggest a simpler alternative.

Experimental measurements are of a series of concentrations of two monoenes, A and B, relative to the concentration of their hydrogenation products, AH_2 and BH_2. In the computer-assisted analysis this data is used to construct a graph of the mole fraction of B in the mixture of B and BH_2 vs. the average number of double bonds remaining per molecule in the mixture of A and AH_2. The inefficiency of this analysis is easily demonstrated for the case where hydrogenation of A and B can be represented as $A + H_2 \xrightarrow{k} AH_2$ and $B + H_2 \xrightarrow{k'} BH_2$; that is, where there is no equilibrium between A and B, nor any other competing reactions.

In this case the first order rate equations (assuming a large excess of hydrogen) may be written

$$[A] = [A]_o \exp(-kt) \qquad [1]$$
$$[B] = [B]_o \exp(-k't) \qquad [2]$$

where $[A]_o$ and $[B]_o$ are the initial concentrations of A and B. From the stoichiometry of the reactions

$$[A]_o = [A] + [AH_2] \qquad [3]$$
$$[B]_o = [B] + [BH_2] \qquad [4]$$

hence, at a particular time after the start of the reaction the mole fractions of A and B are

$$X_A = [A]/[A] + [AH_2] = [A]/[A]_o \qquad [5]$$
$$X_B = [B]/[B] + [BH_2] = [B]/[B]_o \qquad [6]$$

The average number of double bonds per molecule in the mixture of A and AH_2 is equivalent to the mole fraction of A, or X_A. Thus the experimental data are converted into a graph of X_B vs. X_A. From equations [1] and [2] combined with [5] and [6], we obtain

$$X_B/X_A = \exp(-k't)/\exp(-kt) = \exp(k-k')t \qquad [7]$$

so that a graph of X_B vs. X_A will not be linear but show an exponential dependence of X_B upon t and upon X_A. In the method of Scholfield et al. the ratio of k'/k is varied until the sum of (distance)^2 of experimental X_B values from the calculated X_B vs. X_A curve is minimized. Presumably all points are given equal weight in this calculation, but at small values of t, X_B vs. X_A will be negligibly different from unity, no matter what the ratio of k' to k, while at increasing hydrogenation times the value of k'/k becomes increasingly important. If no account is taken of this, the least squares fit is inaccurate, while it is difficult to conceive of a suitable scheme for statistical weighting of the points.

A simpler approach starts by taking logarithms of both sides of equations [1] and [2] to give

$$2.303 \log [A]/[A]_o = -kt \qquad [8]$$
$$\text{and} \qquad 2.303 \log [B]/[B]_o = -k't \qquad [9]$$

The ratio of equations [8] and [9] gives

$$\log [B]/[B]_o /\log [A]/[A]_o = k'/k \qquad [10].$$

Substituting for $[B]/[B]_o$ and $[A]/[A]_o$ from equations [5] and [6], this can be written

$$\log X_B/\log X_A = k'/k \qquad [11]$$

From equation [11] it is evident that a plot of $\log X_B$ vs. $\log X_A$ should be linear. Each point on this plot has the same statistical weight, and least squares fitting is straightforward, with the ratio of rate constants easily calculated from this least squares treatment.

Computer analysis would be useful if there were other reactions competitive with the two reactions discussed, but in any case a simple plot of $\log X_B$ vs. $\log X_A$ should provide an initial value of k'/k for use in this calculation.

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