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USES AND ANALYSES OF CURTIN-HAMMETT/WINSTEIN-HOLNESS SYSTEMS INVOLVING SECOND ORDER REACTIONS[1]

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Abstract—The Curtin-Hammett (C-H) principle and the Winstein-Holness (W-H) equation approximate the product ratio and overall rate constant of reaction for systems involving a starting material which exists in two forms, each of which reacts via first-order kinetics to give a different product. The C-H/W-H approximations are valid when the rates of isomer interconversion are significantly faster than the rates of product formation. The present treatment encompasses non-first-order reactions to product. A numerical predictor-corrector technique is used to show (1) that relative reagent concentration can affect both the product ratio and the observed rates of product formation; (2) that the absolute concentration of reagent and substrate can affect the kinetics; and (3) that factors (1) and (2) above can affect the validity of the C-H/W-H approximations for non-first-order C-H/W-H schemes.

Scheme I generalizes the kinetic system involving a starting material which exists in two forms (e.g. conformational isomers), each of which reacts via second order kinetics to give a different product. Any particular case of this kinetic system can fall into three categories: Case I, when the rate of product formation is significantly faster than the rate of isomer interconversion ($k_{21}[R]$, $k_{34}[R] \gg k_{23}$, k_{32}), then a kinetic quenching situation is obtained; Case II, when $k_{21}[R]$, $k_{34}[R] \ll k_{23}$, k_{32} then the ratio $[A_3]/[A_2]$ is constant throughout the reaction and the product ratio $[A_4]/[A_1]$ and the observed rate constant can be approximated by the well-known Curtin-Hammett[2] (C-H) and Winstein-Holness[3,4] (W-H) expressions (eqn (1)-(2) respectively); and Case III, when $k_{21}[R]$, $k_{34}[R] \sim k_{23}$, k_{32}, then $[A_3]/[A_2]$ and $[A_4]/[A_1]$ are time dependent, the C-H/W-H approximations fail and a more complex mathematical treatment is required to describe the kinetics.

$$A_1 \xleftarrow{k_{21}} R + A_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} A_3 + R \xrightarrow{k_{34}} A_4$$

(1) Curtin-Hammett: $\frac{d[A_4]}{dt} \Big/ \frac{d[A_1]}{dt} = \frac{k_{23}}{k_{32}}\frac{k_{34}}{k_{21}}$

(2) Winstein-Holness: $k_{W-H} = [k_{34}K + k_{21}]/[K + 1]$

where $K = k_{23}/k_{32}$

Scheme I.

Equations (3)-(6) are the four coupled differential equations which describe Scheme I. The rates of formation of products A_1 and A_4 are as indicated by Eqns (3) and (6) respectively, and the ratio of the relative rates of formation of products is given by Eqn (7).

$$\frac{d[A_1]}{dt} = k_{21}[A_2][R] \qquad (3)$$

$$\frac{d[A_2]}{dt} = k_{32}[A_3] - k_{21}[A_2][R] - k_{23}[A_2] \qquad (4)$$

$$\frac{d[A_3]}{dt} = k_{23}[A_2] - k_{34}[A_3][R] - k_{32}[A_3] \qquad (5)$$

$$\frac{d[A_4]}{dt} = k_{34}[A_3][R] \qquad (6)$$

$$\frac{d[A_4]}{dt} \Big/ \frac{d[A_1]}{dt} = \frac{k_{34}[A_3][R]}{k_{21}[A_2][R]} = \frac{k_{34}[A_3]}{k_{21}[A_2]} \qquad (7)$$

The appearance of the term $[R]$ in both the numerator and the denominator of Eqn (7) allows for its subsequent cancellation, thereby *apparently* removing the functional dependence of $[A_4]/[A_1]$ on $[R]$. However, this approximation is valid only if $[A_3]/[A_2] = K$ throughout the course of the reaction. Alternatively, the value of $[A_3]/[A_2]$ may be time dependent, in which case $[R]$ does appear implicitly in the time dependent description of both $A_2(t)$ and $A_3(t)$. Hence, the product ratio $[A_4]/[A_1]$ will be dependent on the concentration of the reagent, $[R]$. We will now demonstrate that the relative concentration of R with respect to substrate (i.e. $[R]_0/([A_2]_0 + [A_3]_0)$) and the absolute concentrations of reagent and substrate can control the product ratio and affect the validity of the C-H/W-H approximations for Scheme I kinetics.

RESULTS AND DISCUSSION

Case III above can be subclassified into two categories: Case III-*A*, for which $k_{21}[R]$, $K_{34}[R] \sim k_{23}$, k_{32} and $[R]_0 \gg [A_2]_0 + [A_3]_0$, then Scheme I kinetics can be approximated by Scheme II using the standard pseudo-first order approximation. Scheme II represents the first-order C-H/W-H kinetic situation,[5] and the exact, analytical solution to this kinetic system has been described and evaluated in detail.[3] In addition, an analytical expression for $[A_4]/[A_1]$ for Scheme II kinetics has been derived at reaction completion when $[A_3]_0/[A_2]_0 = k_{23}/k_{32}$.[6] Thus, Case III-*A* situations can be treated in a straightforward manner by using treatments developed for Scheme II systems.

$$A_1 \xleftarrow{k_{21}} A_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} A_3 \xrightarrow{k_{34}} A_4$$

Scheme II.

Case III-*B* is obtained when $k_{21}[R]$, $k_{34}[R] \sim k_{23}$, k_{32} and $[R]_0 \sim [A_2]_0 + [A_3]_0$. While in principle an exact solution for Case III-*B* can be found which expresses $A_i(t)$ in terms of power series expansions of k_{ij}, we have chosen to evaluate Case III-*B* examples using numerical techniques, either Predictor–Corrector or Runge–Kutta methods.[7] While both of these techniques are less accurate than an exact analytical solution, the accuracy of the Predictor–Corrector procedure can be as good as desired and the maximum error associated with all calculations can be readily obtained.[7c]

To exemplify some of the characteristics of Scheme II kinetics, consider the alkylation of a hypothetical aziridine with a highly active alkylating agent, e.g. methyl fluorosulfonate (see Scheme III).[8] One can approximate an inversion rate constant[9] ($k_{\text{inv}} \sim 1\text{–}100\ \text{sec}^{-1}$) and an alkylation rate constant[8b,10,11] $k_{\text{alkylation}} \sim 1 \times 10^{-6} - 100\ l\ \text{mol}^{-1}\ \text{sec}^{-1}$) for aziridines. In our example, we have set the alkylation rate constant ($k_{2\to1}$) from the more stable isomer **2** to be smaller than the corresponding alkylation rate constant ($k_{3\to4}$) from the less stable isomer **3**. This is consistent with our findings for a wide range of 1-alkyl-2-arylazacycloalkanes.[12]

Figure 1 shows the product ratio [4]/[1] as a function of percent reaction for a range of relative concentrations of $[R]_0$:$\{[2]_0 + [3]_0\}$ where the subscript "0" indicates initial concentration. Note that the initial concentration of substrate is 1×10^{-4} M and that the range of reagent : substrate concentrations covers four orders of magnitude, i.e. reagent concentration varies from 1 M to 1×10^{-4} M. While the mathematical treatment can be extended for other values of the ratio $[R]_0$:$\{[2]_0 + [3]_0\}$, Fig. 1 illustrates only those conditions which are typically experimentally realistic.

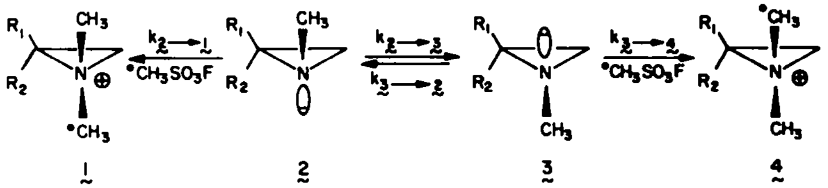
A number of important observations can be made from Fig. 1.

(1) The product ratio [4]/[1] is clearly dependent on the relative concentration of reagent [*R*].

(2) The product ratio is time (and percentage reaction) dependent, and this dependency increases as the relative concentration of reagent [*R*] increases. Using the criterion proposed previously for non-C-H/W-H behavior (5% deviation from the approximations),[3] it can be seen that non-C-H/W-H behavior is observed when the reagent concentration is greater than *ca.* one hundred times substrate concentration. For lower reagent concentration, [4]/[1] is time independent, i.e. those conditions satisfy the C-H/W-H approximations. These points reflect the role that [*R*] plays in determining the rates of product formation (see eqns (3) and (6)).

(3) As the ratio of reagent to substrate increases, the final value of [4]/[1] tends toward the limiting value indicating in Fig. 1. This value essentially represents a kinetic quenching situation[3] in which the rate of product formation is significantly increased by the enormous concentration of reagent even though the actual rate constant or product formation is not exceptionally large.

(4) When [*R*] is significantly concentration limiting



Scheme III.

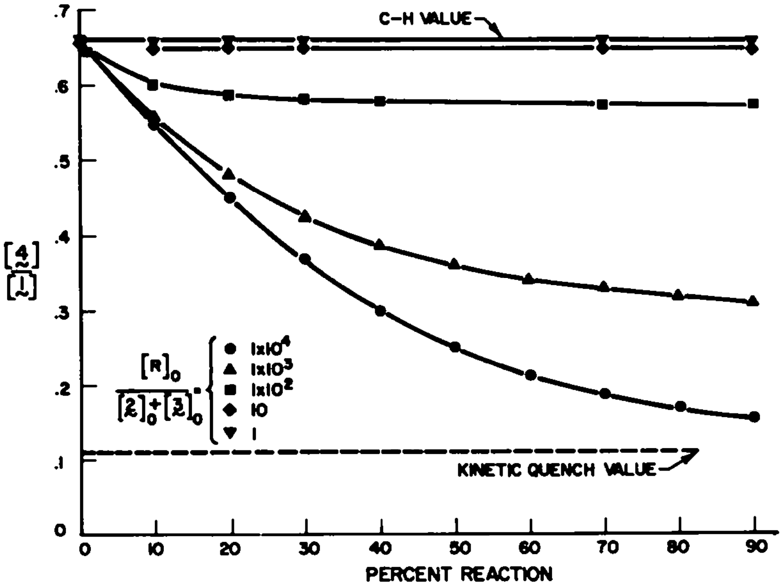


Fig. 1. Calculated values for the product ratio [4]/[1], for Scheme III as a function of initial relative concentration of reagent *R*. Note that the subscript "0" denotes initial conditions. In this example, $k_{2\to1} = 16.7\ l\ \text{mol}^{-1}\ \text{sec}^{-1}$, $k_{2\to3} = 0.55\ \text{sec}^{-1}$, $k_{3\to2} = 5.0\ \text{sec}^{-1}$ and $k_{3\to4} = 100\ l\ \text{mol}^{-1}\ \text{sec}^{-1}$, $\{[2]_0 + [3]_0\} = 1 \times 10^{-4}$ M.

[4]/[1] deviates only slightly from the C–H value. In these instances, however, the percentage reaction based on substrate consumed may be quite small. Thus, the family of curves generated for the dependency of [4]/[1] on relative reagent concentration has two distinct boundaries: the C–H limiting value for the low reagent concentrations and the kinetic quenching limit for large reagent concentration conditions.

In addition to affecting the values of [4]/[1] in Scheme III (or A_4/A_1 in Scheme I), $[R]$ can also affect the rate of product formation. Winstein–Holness kinetics are affected since $k_{W-H} = \Sigma n_i k_i [R]$ where n_i, k_i and $[R]$ are the mole fractions, rate constants for product formation and reagent concentration (see above) for reacting species A_i.[5] Examination of a number of time:percent reaction dependencies indicate that as the concentration of R decreases, the initial rates of product formation become more dependent on $[R]$. In these instances, increasing $[R]$ by one order of magnitude decreases the time required to reach a specific percentage reaction by *ca* one order of magnitude.

Another interesting complexity of Scheme I kinetics is illustrated in Fig. 2 which plots the product ratio [4]/[1] as a function of initial concentration of substrate $[2]_0 + [3]_0$ for a series of initial substrate:reagent values. For any given initial value of $[R]_0:\{[2]_0 + [3]_0\}$, as the absolute concentration of substrate and reagent decreases, the ratio of product [4]/[1] tends toward the Curtin–Hammett value. This is because the k_{21} and k_{34} terms in eqns (4) and (5) respectively become less and less important. That is, significantly decreasing the substrate and reagent concentration for a Scheme I system allows that system to be approximated by Scheme II kinetics.

Thus, Fig. 2 indicates two boundary conditions, the Curtin–Hammett value as the upper limit and the kinetic quenching value as the lower limit. These boundaries are identical to those found for the relationships illustrated in Fig. 1, and this is to be expected since Fig. 1–2 are intimately related to each other.

Literature examples

There are numerous examples in the literature which follow Scheme I kinetics. Complete analysis of these systems involves the experimental determination of the four rate constants. When the rate of product formation is either much faster[13] or much slower[12a,14] than the rate of isomer interconversion (see Case I and Case II, respectively), two experiments are required. First, determination of k_{23}, k_{32} can be made in an independent (of Scheme I) experiment, i.e. an experiment involving only the interconversion of A_2 and A_3 ($A_2 \rightleftarrows A_3$). Then, k_{21}, k_{34} can be determined by analysis of a kinetic expression much simpler than that required for the solution of Scheme I kinetics. On the other hand, when the rates of product formation and isomer interconversion are of the same order of magnitude[15,16] (Case III), k_{21} and k_{34} can only be determined by a complete evaluation of the total Scheme I kinetic system. This requires acquisition and analysis of time:concentration data for all the components of the system, A_i and R.

In cases such as these where the rates of interconversion are proposed to be of the same order of magnitude or slower than the rates of reaction, the experimental determination of the concentration dependencies of the product ratio would be a simple handle on the kinetics. For example, one could determine information regarding the relative magnitudes of k_{23}, k_{32} with respect to k_{21}, k_{34} for any particular system by looking for boundary conditions for the product ratio A_4/A_1 by varying either the ratio of reagent:substrate (Fig. 1) or the concentration of substrate and reagent simultaneously (Fig. 2).

There are examples in the literature of Scheme I kinetics where this type of analysis would be worthwhile. Hydroboration is a reaction which has been cited to be faster than a variety of conformational interconversions in a number of systems.[15a,b,e] A knowledge of rates of isomer interconversion and time:concentration data would allow the determination of the rate constants of

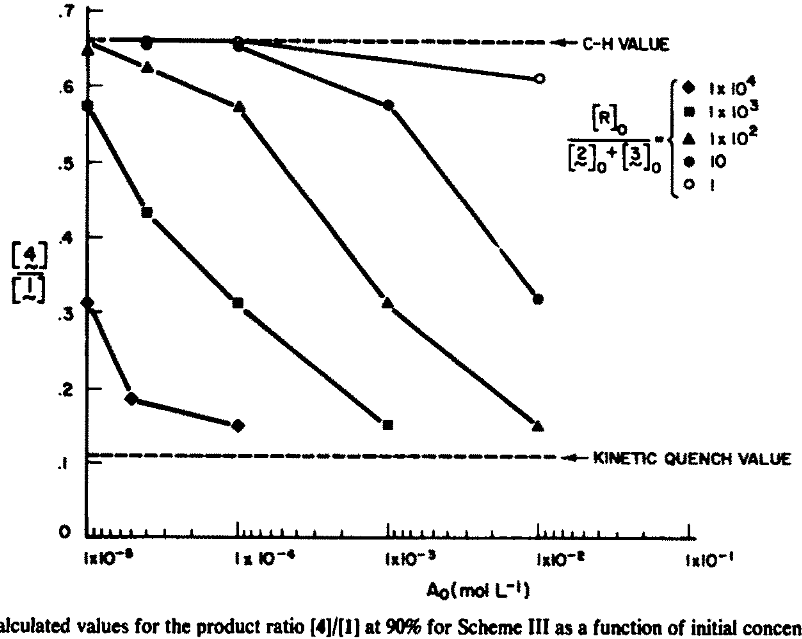
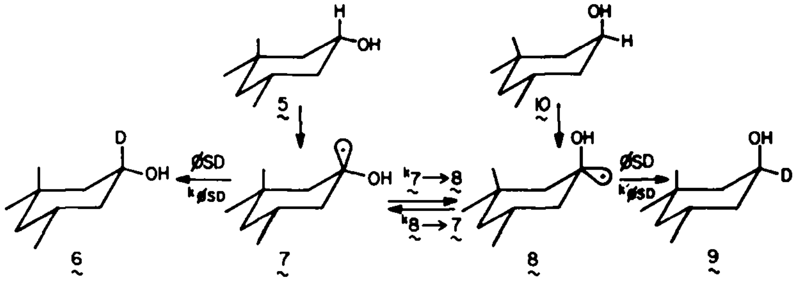


Fig. 2. Calculated values for the product ratio [4]/[1] at 90% for Scheme III as a function of initial concentration of substrate, $\{[2]_0 + [3]_0\}$. See Fig. 1 caption for rate constant information. The family of curves represents constant $[R]_0/\{[2]_0 + [3]_0\}$ values.

reaction (k_{21} and k_{34} of Scheme I) as exemplified above. However, obtaining this information is an imposing experimental problem, as the reactions are undoubtedly quite fast. On the other hand, the qualitative estimates of the relative reates of conformational interconversion vs reaction could be evaluated more simply by examination of the concentration dependencies similar to those shown in Fig. 1, 2. In any event, the complexities of Scheme I kinetics make it evident that little information with regard to the rate constants can be had without time:concentration date. Similar considerations obtain for the reaction of flexible olefins with singlet oxygen[15c] and the ring-opening of *gem*-dichlorocyclopropyl ethers.[15d]

We are unaware of any treatment of a Case III kinetic system involving the analysis of time:concentration data. Examples of steady state treatments of complex Scheme I systems are available, however. For example, Lattes, *et al.* have recently applied steady state techniques to analyze the photoreduction of cyclohexanones.[16] The complexities of the kinetic scheme preclude a full discussion; however, it is worthwhile to focus on one aspect of his analysis. Utilizing steady state approximation for a complex kinetic scheme requires a number of simplifying assumptions. One such assumption involved a comparison of the configurational stability of a pyramidyl cyclohexanol radical with its rate of abstraction of deuterium from a deuterated alcohol (see Scheme IV).



Scheme IV

Lattes observes[16] net retention of configuration starting from either **5** or **10**, and calculates the ratio of the rates of inversion, $k_{7\to8}$ and $k_{8\to7}$, using eqn (8).[17]

$$\frac{k_{8\to7}}{k_{7\to8}} = \frac{[\mathbf{6}]}{[\mathbf{9}]\text{From } \mathbf{5}} \times \frac{[\mathbf{9}]}{[\mathbf{6}]\text{From } \mathbf{10}} \qquad (8)$$

The derivation of eqn (8) is not given but results[18,19] from approximations similar to those made by Lattes for more complex Scheme IV kinetics. Two boundary conditions exist for Scheme IV chemistry. (1) The rates of the deuterium abstraction reactions could be very much faster than the rates of inversion, as assumed by Lattes. However, since partitioning is observed, i.e. starting from **5** (or **10**) *does* lead to some **9** (or **6**), postulate (1) is not valid. (2) Alternatively, the rates of the abstraction reactions could be much slower than the rates of inversion. If this were the case, then the selectivity observed would be the same regardless of whether **5** or **10** were the starting material. As the product ratio [**9**]/[**6**] is dependent on the starting isomer ([**9**]/[**6**] = 5 ± 1 from **10** and 11 ± 1 from **5**), postulate (2) is not valid. Since neither of the two extreme boundary conditions plays a dominant role in Scheme IV kinetics, evaluation of this system requires more complex kinetic analyses of the type discussed above for Scheme I situations.

It is important to note that while the rate constants of deuterium abstraction ($k_{\phi SD}$) may be much larger than the rate constants for inversion ($k_{8\to7}$ and $k_{7\to8}$), the low concentration of ϕSD decreases the rate or velocity of the abstraction reaction considerably. This very low concentration of ϕSD is caused by its formation only in equivalent molar amounts during the course of the reaction sequence. In addition, since [ϕSD] is likely to be time dependent, the velocity of the abstraction reaction will also be time dependent. Hence, the time dependency of the product ratio [**6**]/[**9**] is likely to be as complex as those illustrated by Fig. 1, 2.

As can be seen from the type of results shown in Figs. 1, 2, product stereoselectivity in any complex reaction scheme should not be approximated by steady state means without subsequently evaluating the steady state approximations with the derived rate constant and experimental product ratio data. That is, proper use of steady state analysis dictates investigation of the validity of the assumptions made, e.g. what is the time dependency of the product stereoselectivity? Thus, the complexities shown above for Scheme I kinetics (see Figs. 1 and 2) clearly indicate the perils of indescriminate use of simplifying assumptions in these systems.

SUMMARY

In conclusion, the reagent concentration, [R], at fixed initial substrate concentration, {$[A_2]_0 + [A_3]_0$}, can affect both product ratio A_4/A_1 and total observed rates of product formation, $k_{W\text{-}H}$, for non-C-H/W-H Scheme I systems. In addition, the absolute concentration of reagent and substrate can affect both A_4/A_1 and $k_{W\text{-}H}$. This indicates that in Scheme I non-C-H/W-H systems, product distribution can be controlled by relative reagent concentration as well as by absolute concentration of reagent and substrate. In addition, the C-H/W-H approximations are valid when the rates of isomer interconversion are greater than the rates of product formation: thus, the absolute and relative concentrations of substrate(s) and reagent can affect the validity of the C-H/W-H approximation (eqn (1)-(2)) since increasing these concentrations will increase the overall rate of product formation. Lastly, the validity of these analyses is dependent on the correctness of the kinetic scheme in describing the observed reactions. For example, more complex kinetics would result if the reagent were added to the substrate during the course of the reaction rather than all at once as presupposed in the present treatment.

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This referee has also requested information regarding the maximum calculation error for the numerical methods used in this work. Neither the Euler procedure, which was used in the early stages of our work, nor the Runge–Kutta procedure gives a mathematically calculable estimate of the error associated with the numerical approximation. As a check on these methods, we have routinely compared the calculated results for a set of rate constants and reagent concentrations using one choice of $\Delta\tau_1$ (the time increment) with the calculated results for the same set of rate constants and reagent concentrations using a smaller time increment $\Delta\tau_2$. Usually, we chose $\Delta\tau_2 = 0.1\ (\Delta\tau_1)$. If the time:concentration calculations were found to be identical, the calculation errors were assumed smaller than the number of significant figures obtained in the computer results. The Predictor–Corrector method is superior to the Euler and Runge–Kutta methods because it not only calculates the maximum error associated with each numerical step but also utilizes the given information and the previous calculated steps to best calculate the next step. The major disadvantage of the Predictor–Corrector procedure is the significantly greater computation time required. In some of our work, we also found that the Predictor–Corrector technique would not converge even at very small time increments. To go to even smaller increments was not always feasible from a computational point-of-view, and the Runge–Kutta procedure was substituted. For all of our runs using the Predictor–Corrector method, our total cumulative error (relative) was four orders of magnitude less than the calculated values; [d] C. W. Childs, P. S. Hallman and D. D. Perrin, *Talanta*, **16**, 1119 (1969) and Refs cited therein; and [e] I. D. Gay, *J. Phys. Chem.*, **75**, 1610 (1971).

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[19] Note added in proof. We thank Prof. A. Lattes for additional communications dated 21 June 1979 and 3 October 1979 which indicate full agreement with the analysis presented herein.