complex of enzyme, NADH, and α-ketoglutarate, previously characterized at equilibrium (7).

Using these powerful theoretical tools, coupling the results of transient kinetics with those obtained at equilibrium, and extending them over a range of solvents and temperatures, one can construct a detailed picture of biochemical mechanism, complete with both free energy and enthalpy characterization of important reaction intermediates.

This work was supported in part by grants from the National Science Foundation (PCM75-17107) and from the General Medicine Institute of the National Institutes of Health (GM15188).

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A METHOD FOR DETERMINING THE KINETIC TYPE OF FAST KINETIC DATA

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Several well-established methods exist for the treatment of data obtained by fast kinetic techniques, whereby the appropriate kinetic parameters (e.g., rate constants) may be extracted. Typically, these methods involve an initial assumption as to the appropriate type of kinetics, which is then employed to fit the corresponding kinetic equations to the data. Particularly in the case of pulse radiolysis and flash photolysis, the frequent occurrence of mixed-order processes (whether independent or competing, growth or decay), of simultaneous detection of more than one species, and of residual base-line concentrations often make it difficult to choose the correct initial assumption for data analysis.

Furthermore, a given data set can frequently be fit with comparable success by more than one type of kinetics, making it necessary to vary the experimental conditions to distinguish among the possible analyses. The systematic application of several different data reduction techniques to several sets of data becomes tedious, and the sheer volume of results thus obtained may actually obscure rather than clarify the correct solution to the problem.

We present a data reduction technique applicable without any initial assumptions regarding the kinetics involved, which produces a graphical output from whose shape the type of kinetic analysis appropriate to the data can, in most cases, be determined by simple visual examination. This technique is intended as a preliminary to the fitting and extraction of kinetic parameters. Let $V(t)$ be the data trace proportional to concentration, and let $\mathrm{d}/\mathrm{d}t\,[\log(V(t_0)/V(t)0]$ be plotted vs. $V(t)$. The resulting transform is linear in the special case of competing first- and second-order processes with the intercept and slope giving the first- and second order-rate constants, respectively (1, 2). For more complicated kinetics this transform may be sigmoid or otherwise curved, but it is generally quite distinctive.

Computation of the transform described involves the difficult problem of evaluating the derivative of experimental data containing noise. Acceptable results were obtained by first applying a simple linear filter to the function to be differentiated. Then a least-squares fit of the first eight Chebyshev polynomials was obtained and differentiated analytically.

Results are presented for synthetic data of various types, and the limiting signal-to-noise ratio for successful analysis is examined. The method is also applied to experimental data and the usefulness of families of such curves, corresponding to different experimental conditions, is illustrated.

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THE EFFECT OF PRETREATMENT WITH CALCIUM AND MAGNESIUM IONS ON PHOSPHOENZYME FORMATION BY SARCOPLASMIC RETICULUM ATPase

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It has previously been shown (1, 2) that pretreatment of $(Na^+ + K^+)$ATPase with K^+ (10–20 mM) before the addition of Na^+ and ATP slows the rate of phosphoenzyme formation and reduces the early phosphate "burst." These effects have been explained