centrations suggests that the first excited electronic state is not involved in the photoreduction (compare appendix of ref. 10). Since small amounts of *p*-phenylenediamine retard the reaction, a long-lived excited state of the dye must be the chemically reactive species. From the data of Fig. 3 and the theoretical frequency of encounters between diffusing molecules in solution (6.6×10^9 sec.$^{-1}$ liter mole^{-1} in water at room temperature[11]) we calculate that the life-time of this metastable excited species is equal to or greater than 8.7×10^{-5} sec., *i.e.*, about 10^5 times longer than the first excited electronic state. In all respects the kinetics of the photoreduction of methylene blue resemble that of eosin using conventional reducing agents.[11] The deviation from linearity at very high EDTA concentrations can be attributed to direct deactivation of the first electronically excited state and is manifested in fluorescence quenching.

Photoöxidation of the leuco dye by near ultraviolet involves excited states of the leuco dye molecule. The leuco dye absorbs in the near ultraviolet and exhibits a bright yellow fluorescence and in rigid media an intense greenish phosphorescence. The rate of photoöxidation is *p*H dependent and increases with hydrogen ion concentration. For this reason photorecovery of leuco dye in the presence of EDTA is more rapid at *p*H 7 than at *p*H 9 although the opposite is the case for photobleaching. Leuco dye made with acidic reductants such as ascorbic acid or stannous chloride exhibit a greater quantum yield of photorecovery.[5]

BROOKLYN, N. Y.

[10] M. Pestemer, *Z. Elektrochem.*, **58**, 121 (1954).

[11] G. Oster and A. H. Adelman, THIS JOURNAL, **78**, 913 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AND THE RAND CORPORATION]

Determination of the Rate Constant Ratio in Competitive Consecutive Second-order Reactions

BY W. G. McMILLAN

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The ratio of the rate equations for a pair of competitive consecutive second-order reactions is solved in such a way as to yield the rate constant ratio as an implicit function of any two simultaneous concentrations.

Several detailed numerical procedures have been given for the experimental determination of the individual rate constants k_1 and k_2 in kinetic systems consisting of two competitive and consecutive irreversible second-order reactions

$$A + B \xrightarrow{k_1} C + E$$

$$A + C \xrightarrow{k_2} D + F$$

Interest in this system arose originally in connection with those reactions, such as the successive saponification of dibasic esters, wherein the concentration of component A is easily followed titrimetrically. Thus, the previous kinetic treatments given by Ingold,[1] Ritchie,[2] Westheimer, Jones and Lad,[3] French,[4] and most recently by Frost[5-7] and co-workers, have aimed at extracting the values of k_1 and k_2 solely from a knowledge of the concentration A(t) of component A as a function of time. Although considerable ingenuity has been shown in the solution of this rather difficult problem, the solution has been given in detail only for the case of equivalent initial reactant concentrations (*i.e.*, $A_0 = 2B_0$), or for a limited range of the extent of reaction.

It is the purpose of the present note to solve the much simpler problem of obtaining the ratio $\kappa = k_2/k_1$ of the two rate constants from a knowledge of the concentrations of two components at a single time. This case assumes greater relevance in view of the increasingly powerful analytical methods whereby one can often directly determine the concentration of products and reactants other than A. Moreover, the restriction to equivalent initial concentrations will not be necessary here. Although the procedure to be given is much simpler than in the general case, it also accomplishes less in providing only the ratio κ rather than the values of the individual rate constants k_1 and k_2.

The rates of change of the concentrations B and C are

$$dB/dt = -k_1AB \qquad (1)$$

and

$$dC/dt = k_1A(B - \kappa C) \qquad (2)$$

In terms of reduced concentrations, defined by

$$\beta = B/B_0 \qquad (3a)$$

$$\gamma = C/B_0 \qquad (b)$$

the ratio of eq. 2 to 1 becomes

$$d\gamma/d\beta = (\kappa\gamma - \beta)/\beta \qquad (4)$$

By changing to a new pair of variables (β, γ/β), this homogeneous differential equation is solved easily, after which the original variables are restored. Integration between the initial (1,0) and final (β,γ) values of the original variables then gives

$$\kappa \ln \beta = \ln[\beta + (1 - \kappa)\gamma] \qquad (5)$$

or

$$\gamma = \beta(1 - \beta^{\kappa-1})/(\kappa - 1) \qquad (6)$$

[1] C. K. Ingold, *J. Chem. Soc.*, 2170 (1931).

[2] M. Ritchie, *ibid.*, 3112 (1931).

[3] F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

[4] D. French, THIS JOURNAL, **72**, 4806 (1950).

[5] W. C. Schwemer and A. A. Frost, *ibid.*, **73**, 4541 (1951).

[6] A. A. Frost and W. C. Schwemer, *ibid.*, **74**, 1268 (1952).

[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 165ff.

This result is similar to eq. 10 of Frost and Schwemer,[6] but without their restriction.

For any measured pair (β,γ) of experimental concentrations, one may easily find the value of κ which satisfies eq. 5 as accurately as necessary, either by numerical inspection or by direct determination of the intersection of the left and right hand sides, considered as functions of κ for the given values of the parameters (β,γ). As an aid in determining the approximate value of κ, Fig. 1 shows lines of constant κ in the β,γ-plane. In many cases, interpolation on this graph may provide sufficient accuracy, especially if more than one experimental (β,γ) pair is available.

For sufficiently small κ, say less than 0.05, eq. 5 permits of the explicit approximate solution

$$\kappa \approx [\ln(\beta + \gamma)]/[\ln \beta + \gamma/(\beta + \gamma)] \qquad (7)$$

Finally, it should be noted that the concentrations of any pair could have been used, in view of the stoichiometric relations

$$2\beta + \gamma = 2 - (A_0 - A)/B_0 \qquad (8a)$$

and

$$\gamma = (A_0 - A - 2D)/B_0 \qquad (b)$$

I have to thank Professor D. J. Cram of the Department of Chemistry, University of California at Los Angeles, for calling my attention to this problem.

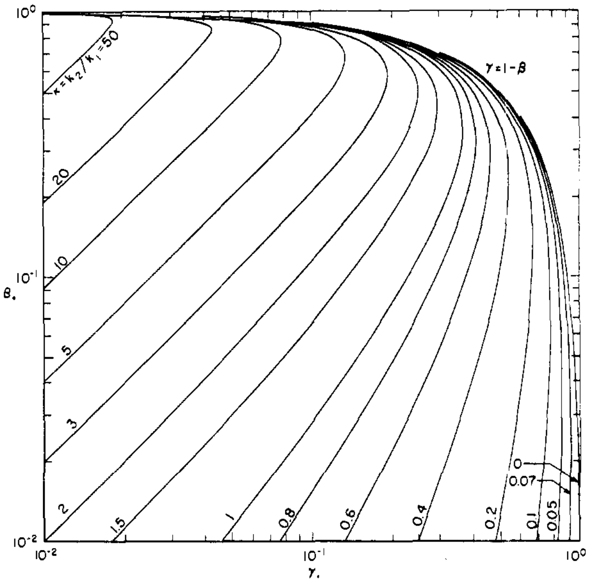

Fig. 1.—Relative extents of the two reactions for given values of the rate constant ratio κ. The envelope, $\kappa = 0$, has the equation $\gamma = 1 - \beta$.

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Molecular Complexes and Their Spectra. VII. The Spectrophotometric Study of Molecular Complexes in Solution; Contact Charge-transfer Spectra[1]

BY L. E. ORGEL AND R. S. MULLIKEN

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The application of spectrophotometric techniques to the determination of the equilibrium constants and extinction coefficients of molecular complexes in solution is discussed and complications due to the presence of several 1:1 complexes with different orientations and to "contact" charge-transfer absorption by pairs of molecules contiguous to each other are emphasized. It is pointed out that values of equilibrium constants and extinction coefficients for loose complexes as determined by the method of Benesi and Hildebrand need reinterpretation or revision. Absorption by pairs of molecules in the complete range of cases from statistical contacts to 1:1 complexes is discussed in terms of a simple model. The resulting equations are used to show that the apparent anomaly of decreasing extinction coefficient with increasing methylation in the charge-transfer spectra of the iodine complexes of the methylated benzenes can be removed when it is recognized that a considerable part of the absorption in the more loosely associated cases is probably due to contact pairs rather than complexes. Nitro compound complexes are also discussed qualitatively. We believe that the simple model used here helps to clarify some long-standing difficulties, emphasized especially by Bayliss, in the attribution of spectral changes in solution to the formation of loose complexes.

Isomerism in 1–1 Complex Formation[2]

In this paper we shall discuss the interpretation of measurements of the absorption spectra of weak complexes, particularly charge-transfer complexes, in solution. We shall be concerned with two factors[2] which may complicate the analysis of the experimental data, namely, the existence of several geometrically and/or electronically different 1:1 complexes in equilibrium, and the occurrence of contact charge-transfer absorption. (What we mean by "several different 1:1 complexes in equilibrium" is explained near the end of this Section.)

The usual method of determining the equilibrium constant and extinction coefficient for a 1:1 complex in solution is the one first proposed by Benesi and Hildebrand.[3] They use the mass action relation

$$K = x_C/(x_D - x_C)(x_A - x_C) \qquad (1)$$

where x_C is the mole fraction of complex; x_D and x_A, respectively, are the total (*i.e.*, complexed plus uncomplexed) mole fractions of the donor and ac-

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[1] This work was assisted by the Office of Ordnance Research under Project TB2-0001(505) of Contract DA-11-022-ORD-1002 with The University of Chicago.

[2] Attention already has been called briefly to the effects of the presence of more than one 1:1 complex by E. Grunwald and J. E. Leffler (see Ross, Labes and Schwarz, THIS JOURNAL, **78**, 343 (1956), footnote 2).

[3] H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949). For an improved procedure, and other comments, see R. L. Scott, ref 9 below.