Appendix

The conjugation energy (c.e.) for the interior atoms in the C_n chain is obtained from the difference in c.e. for allene and ethylene with a correction for compressional energy corresponding to contraction from the standard double bond to the 1.28 Å. bond assumed for the chain.

The c.e. is calculated following the M.R.B. method and the Lofthus modification of that method. M.R.B.[14] assume zero overlap integral, a reference double bond of 1.33 Å. (ethylene double bond) and a standard resonance integral $\beta_0 = -44.5$ kcal./mole. Lofthus[15] uses overlap integrals calculated with Slater or S.C.F. atomic orbitals. The reference double bond distance is 1.353 A. The β_0 values are -81 and -102 kcal./mole for Slater orbitals or S.C.F. orbitals, respectively.

An additional correction of $0.5 \beta_0$ is introduced by Lofthus to account for the different electronegativity of the terminal hydrogen group as compared to the carbon atom. The secular equation 1 for allene and ethylene is solved for localized and delocalized bonds. The values for the β_0 coefficients and for conjugation energy are given in Table VIII.

Compressional energies are obtained from a Morse potential assuming a dissociation energy $D = 141.5$ kcal./mole and a bond force constant of 8.2×10^5 dyne cm.$^{-1}$.

The contribution to $\Delta H_0{}^0$ of formation of the hypothetical C_n with localized bonds per interior carbon atom is then the difference in $\Delta H_0{}^0$ of formation[16] between allene and ethylene (33.178 kcal./

TABLE VIII

ORBITAL AND CONJUGATION ENERGIES OF ALLENE AND ETHYLENE

Method	Localized M.O. coefficients		Delocalized M.O. coefficients		Conjugation energy
(M.R.B.) Ethylene	4.000	...	4.531	3.531	0.124
Allene	4.000	1.058	4.146	1.023	.444
(L-S) Ethylene	1.275	...	1.508	1.048	.012
Allene	1.277	0.845	1.432	0.710	.121
(L-F) Ethylene	0.945	...	1.177	.718	.008
Allene	0.946	0.770	1.140	.601	.098

mole) corrected for the difference in their conjugation energies and compressional energies. If the compression energy to the 1.28 Å. bond distance of C_3 (and presumably of longer C_n molecules) is added, the final values are 48.323, 43.112 and 43.408 kcal./mole for the (M.R.B.), (L-S) and (L-F) methods. These values are used in the calculations leading to Table I.

BERKELEY, CALIFORNIA

The Method of Continuous Variations for Some Special Types of Reaction

BY MARK M. JONES

An examination has been made of the use of the method of continuous variations for some types of reactions which do not follow the patterns already in the literature. The use of this method to establish the stoichiometry of complexes in solution is warranted in some cases where species are produced in addition to the complex. Its use is also warranted when one of the reactants or the complex is an acid or a base provided that certain restrictions are satisfied. The specific cases considered are: (1) where several species, in addition to the complex, are produced in stoichiometric amounts, (2) where the complex produced is a weak acid (or a weak base) and (3) where one of the reactants is the anion of a weak polyprotic acid or is a weak polybasic species. In many cases it is possible to establish the stoichiometry in a simple manner, while the evaluation of the stability constant of the complex cannot be accomplished using the simple equations given in the literature.

The use of the method of continuous variations (Job's Method) in studying complexes in solution is open to several objections and accompanied by restrictions of a fairly serious nature.[1-3] One of the most serious difficulties facing the prospective user of this method is a very fundamental one. This is the selection of a theoretical treatment from the literature which is based upon a prototype reaction that is similar to the reaction under study. In most cases this is simply not possible. The purpose of this paper is to show how this method may be used to establish the stoichiometry of complexes in some situations where the complex-forming reactions possess complicating features not previously considered. In all of the reactions examined here, only *one* complex may be formed.

For some cases where more than one complex is formed, recourse to the methods presented by Vosburgh[2,4] and by Katzin[5] is possible.

The types of reaction considered in this paper are (1) a complex is formed with the concurrent production of an arbitrarily large number of other species, all formed in stoichiometric amounts; (2) a complex is produced which is a weak monobasic acid; and (3) one of the reactants is the anion of a weak acid or a very similar type of reaction in which one of the reactants is a weak base.

In the derivations given below the usual assumptions are made in setting the concentrations of the various species equal to their activities. A method of correcting for this has been given in a previous paper.[3] The cases given here represent reactions of types which previously have been

(1) F. Woldbye, *Acta Chim. Scand.*, **9**, 299 (1955).

(2) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

(3) M. M. Jones and K. K. Innes, *J. Phys. Chem.*, **62**, 1005 (1958).

(4) R. K. Gould and W. C. Vosburgh, THIS JOURNAL, **64**, 1630 (1942).

(5) L. I. Katzin and E. Gebert, *ibid.*, **72**, 5455, 5459 (1950).

studied experimentally, for example, those between polyhydric coördinating agents and acids such as boric,[6] molybdic[7] and tungstic,[8] or those involving polyfunctional bases.[9]

Case I.—A reaction which proceeds with the formation of a complex *and* an arbitrary number of other substances, all produced in fixed relative amounts, may be represented by the equation

$$A + nB \rightleftarrows AB_n' + dD + eE + fF + \ldots \quad (1)$$
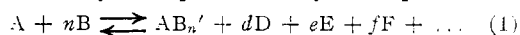
The equations derived below are based on the assumption that D,E,F, etc., represent components of B or A such as H_2O from $A(H_2O)_y^{+z}$ or similar substances. B′ is the portion of B which enters the complex, and one B′ is obtained from each B. This is not a necessary restriction on the treatment, but one dictated by convenience. Analogous equations can be derived for other special relations among B′, D,E,F, etc., and the reactants. Using the same mixing procedure as Vosburgh and Cooper[2] and Job[10] we may write the concentration of the various species after equilibrium has been attained as

$$A = C_1 = M(1 - x) - C_3 \quad (2)$$

$$B = C_2 = Mx - nC_3 \quad (3)$$

$$AB_n' = C_3 \quad (4)$$

$$D = dC_3 \quad (5)$$

$$E = eC_3 \text{ etc.} \quad (6)$$

The equilibrium constant for this reaction will be

$$K = \frac{[AB_n'][D]^d[E]^e[F]^f \ldots}{[A][B]^n} \quad (7)$$

The condition that the products are to be formed in fixed relative proportions allows this to be written as

$$K = \frac{d^d e^e f^f \ldots (C_3)^{1+d+e+f \ldots}}{C_1 \cdot C_2^n} \quad (8)$$

Differentiation of this eq. with respect to x gives

$$\frac{dC_3}{dx}(1 + d + e + f + \ldots) d^d e^e f^f \ldots C_3^{d+e+f+\ldots} \left(\frac{1}{K}\right)$$

$$= \left\{ nC_1C_2^{n-1} \frac{dC_2}{dx} + C_2^n \frac{dC_1}{dx} \right\} \ldots \quad (9)$$

The condition for a maximum concentration of the complex is $dC_3/dx = 0$. This condition means that the term in braces on the right-hand side of eq. 9 must be zero. Such a condition leads to the conclusion that the concentration of the complex will reach a maximum in that solution for which $n = x/(1 - x)$.

The most commonly encountered examples of this type are those in which hydrogen ions are released in stoichiometric amounts as a *strong* acid is formed (*e.g.*, the boric acid–mannitol reaction). These systems may be studied without buffering the system. The use of this method leads to success in some other systems involving

(6) G. Sutra and E. Darmois, *Bull. Soc. Chem. Belg.*, **62**, 104 (1953).

(7) A. Honnelaitre, *Ann. Chem.*, [X] **3**, 5 (1925).

(8) M. Murgier and M. Cordier, *Compt. rend.*, **213**, 729, 836 (1941).

(9) H. B. Jonassen and P. C. Yates, THIS JOURNAL, **74**, 3388 (1952), and other papers in that series.

(10) P. Job, *Compt. rend.*, **180**, 928 (1925). There is considerably greater freedom in the preparation of these solutions than is commonly supposed. See also ref. 3 and S. K. Siddhanta, *J. Indian Chem. Soc.*, **25**, 584 (1948).

metal ions,[11] the chief restriction being that the complex produced must be a *strong* acid.

Case II.—Another type of reaction which is encountered is one in which the complex produced is a weak monobasic acid. In this case the relative amounts of complex and hydrogen ion will *not* be fixed. The equilibria in such a situation will be

$$A + nB \rightleftarrows AB_n^- + H^+ \quad (10)$$

$$HAB_n \rightleftarrows AB_n^- + H^+ \quad (11)$$
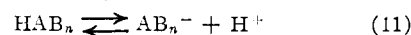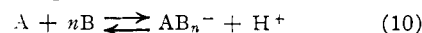
for which the equilibrium constants are

$$K_1 = \frac{[AB_n^-][H^+]}{[A][B]^n} \quad (12)$$

$$K_2 = \frac{[H^+][AB_n^-]}{[HAB_n]} \quad (13)$$

With our solutions prepared in the usual manner we can write the equilibrium concentrations of the various species as

$$[A] = C_1 = M(1 - x) - C_3 \quad (14)$$

$$[B] = C_2 = Mx - nC_3 \quad (15)$$

$$[AB_n^-] = C_3 - [HAB_n] = C_3 - \frac{[H^+][AB_n^-]}{K_2} \quad (16)$$

$$[H^+] = [AB_n^-] \quad (17)$$

From these equations we can now eliminate $[H^+]$ and $[AB_n^-]$ by obtaining an expression for these quantities in terms of K_2 and C_3. This leads to a quadratic equation in $[H^+]$ or $[AB_n^-]$ which is solved to give

$$[AB_n^-] = [H^+] = \frac{-K_2 \pm \sqrt{K_2^2 + 4K_2C_3}}{2} = Z \quad (18)$$

These values now can be used to set up a continuous variations treatment since

$$K_1 = \frac{Z^2}{[A][B]^n} = \frac{Z^2}{C_1 \cdot C_2^n} \quad (19)$$

On differentiating eq. 19 we can obtain the condition for a maximum value of C_3 as

$$\frac{2Z}{K_1} \times \frac{dZ}{dx} = nC_1C_2^{n-1}\frac{dC_2}{dx} + C_2^n \frac{dC_1}{dx} \quad (20)$$

From eq. 31

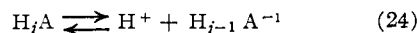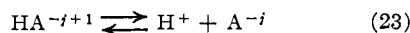$$\frac{dZ}{dx} = \pm \frac{K_2}{\sqrt{K_2^2 + 4K_2C_2}} \times \frac{dC_3}{dx} \quad (21)$$

Here again setting $dC_3/dx = 0$ we get the same conditions for a maximum value of C_3 as were obtained in Case I. By setting the right side of eq. 20 equal to zero and using explicit values for dC_1/dx and dC_2/dx we again get $n = x/(1 - x)$. In this case, however, C_3 is the *total* concentration of complex species present, *i.e.*, $[AB_n^-] + [HAB_n]$. Thus in studying cases of this sort it is necessary to use a physical property of the solution which measures this sum in a suitable manner. To determine the stability constant, K_1, in such a case it is necessary to have information on K_2 and $[H^+]$ or $[AB_n^-]$ in addition to the usual information obtained in a continuous variation study.

Case III.—A final pair of cases represents many of the complexing reactions encountered. In the first example one of the *reactants* is the anion of a

(11) S. N. Banerjee. A. K. Sen Gupta and S. K. Siddhanta, *ibid.*, **35**, 269 (1958); S. K. Siddhanta and S. N. Banerjee, *ibid.*, **35**, 279, 323, 339, 343, 419, 423, 426 (1958).

weak acid. In the second one of the reactants is a weak base. These will be treated separately, though the similarities will be evident.

First type: when one of the reactants is the anion of a weak acid the equilibria in solution will be

$$A^{-i} + nB \rightleftharpoons AB_n \qquad (22)$$

$$HA^{-i+1} \rightleftharpoons H^+ + A^{-i} \qquad (23)$$

$$H_jA \rightleftharpoons H^+ + H_{j-1}A^{-1} \qquad (24)$$

At equilibrium the concentrations of the various species in solutions prepared by the usual method will be

$$[A^{-i}] = C_1 = M(1 - x) - C_3 - \sum_{Z=1}^{Z=j} [H_ZA^{-i+Z}] \qquad (25)$$

$$[B] = C_2 = Mx - nC_3 \qquad (26)$$

$$[AB_n] = C_3 \qquad (27)$$

The equilibrium constants for reactions 22 through 24 will be

$$K_C = \frac{[AB_n]}{[A^{-i}][B^n]} \qquad (28)$$

$$K_1 = \frac{[H^+][A^{-i}]}{[HA^{-i+1}]} \qquad (29)$$

$$K_j = \frac{[H^+][H_{j-1}A^{-i}]}{[H_jA]} \qquad (30)$$

In eq. 25, all the terms in the summation over Z can be expressed in terms of $[A^{-i}]$, $[H^+]$ and the various K_j's. Letting

$$Q = 1 + \sum_{Z=1}^{Z=j} \left(\frac{[H_ZA]}{[A^{-i}]} \right) = 1 + \sum_{Z=1}^{Z=j} \frac{[H^+]^Z}{\prod\limits_{Z=1}^{Z=j} K_i} \qquad (31)$$

then

$$[A^{-i}] = \frac{M(1-x) - C_3}{Q} = C_1 \qquad (32)$$

The condition for a maximum in C_3 then can be obtained by differentiating eq. 21 as

$$nC_1C_2^{n-1} \frac{dC_2}{dx} + C_2^n \frac{dC_1}{dx} = \frac{1}{K_C} \frac{dC_3}{dx} \qquad (33)$$

In this case, $dC_2/dx = M$, but from (32)

$$\frac{dC_1}{dx} \left\{ -MQ - [M(1-x) - C_3] \frac{dQ}{dx} \right\} \Big/ Q^2 \qquad (34)$$

and

$$\frac{dQ}{dx} = \sum_{Z=1}^{Z=j} \frac{[H^+]^{Z-1}}{\prod\limits_{Z=1}^{Z=j} K_i} \frac{d[H^+]}{dx} \qquad (35)$$

The conditions for which C_3 is a maximum are then *not* the same as those found previously and it is necessary to introduce an additional restriction if the method is to be used in the usual fashion.

This additional restriction is that the solutions must be buffered, *i.e.*, $d[H^+]/dx = 0$. In this case dQ/dx will also be zero and our equations will once more reduce to $n = x/(1 - x)$ when C_3 is a maximum. The case of a weak polyfunctional base can be treated in a similar manner with analogous results.

Discussion

Since the method of continuous variations seems to be suitable for studying many types of reactions, it is necessary to inquire more carefully into the cause for its present ill-repute. When this is done it is found that this poor reputation is due chiefly to two factors. The first of these is the application of the method in its simple form to systems where two or more complexes are present. This has been discussed in some detail by Woldbye.[1] The second reason is that many stability constants determined by this method are in very poor agreement with stability constants determined by other methods. The reasons for this can be seen by an examination of some of the methods published for determining equilibrium constants from data obtained in continuous variation studies.

Of eleven[2,5,12-19] of these methods, nine[12-19] can be used only when but a single complex is present and of these only two[18,19] can be used when additional equilibria play an important role. Both of these have been used only with specific examples of case III but can be extended easily to analogous situations. The other seven will give erroneous values for stability constants for reactions of the types examined in this paper. A more reasonable approach requires measurements in addition to those carried out in the continuous variation study itself, *e.g.*, of pH.

In conclusion, the method of continuous variations can be used to establish the stoichiometry of a single complex in many systems where numerous other types of equilibria occur. In the determination of the stability constants for these systems *all* these equilibria must be taken into consideration.

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