and eq. 12

$$k = \frac{\left[\frac{AV}{n_0}\right]^{x-1} \Delta T}{(A - a)^x} \tag{22}$$

These equations clearly indicate why this method is so insensitive to errors. The heat capacity essentially drops out. Slopes, which cannot be accurately measured have only a small effect on the final equation. The cell constant also tends to cancel out. The dominating terms in the equation are the height ($\Delta T$) and remaining area of the curve ($A - a$), both of which can be measured accurately. In view of this fact, one would tend to assign more significance to the points calculated at lower temperatures where the remaining area is large and less susceptible to errors and where the smaller terms have the least influence.

It should be noted that eq. 22 is identical to eq. 19, the rate constant expression in differential enthalpic analysis. This demonstrates that the curves obtained by DTA and DEA are to a good degree of approximation the same.

The exceptional feature of this approach to kinetics is the rapidity with which the measurements are performed. The complete procedure including analysis of the data requires about one day, where a conventional approach may require several weeks to obtain the same data.

**Acknowledgment.**—The support of the U. S. Rubber Company in granting one of the authors (HJB) a fellowship is acknowledged with thanks.

Madison, Wisconsin

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[Contribution from the Chemistry Departments of Illinois Institute of Technology and the University of Michigan]

# The Thermal Decomposition of Chloroform. II. Kinetics[1a]

By George P. Semeluk[1b] and Richard B. Bernstein

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The kinetics of the thermal decomposition of gaseous chloroform and chloroform-*d* have been investigated from 450–525°. At low extent of reaction the rate expression was found to be $-\mathrm{d}/\mathrm{d}t\,[\mathrm{CCl_3H}] = k[\mathrm{CCl_3H}]/(1 + b[\mathrm{HCl}])^{1/2}$. The activation energy based on initial slopes was 37.2 ± 2.0 kcal./mole for chloroform and 37.5 ± 2.0 kcal./mole for chloroform-*d*. The frequency factor was $6.3 \times 10^8$ sec.$^{-1}$ in both cases. A mechanism satisfactory for low extent of reaction is (1) $\mathrm{CCl_3H \rightarrow CCl_2H\cdot + Cl\cdot}$; (2) $\mathrm{Cl\cdot + CCl_3H \rightleftharpoons HCl + CCl_3}$; (3) $\mathrm{CCl_3\cdot + Cl\cdot \rightarrow CCl_4\cdot}$; (4) $\mathrm{CCl_3\cdot \rightarrow CCl_2: + Cl\cdot}$; (5) $\mathrm{CCl_2: + CCl_3H \rightarrow C_2Cl_4 + HCl}$. From the present data and auxiliary information in the literature the upper limit for the C-Cl bond dissociation energy in chloroform is estimated to be $E_1 \leq 72$ kcal./mole.

In Part I[2] the experimental methods were described and the distribution of products in the pyrolysis of chloroform was discussed. The results of the kinetic studies are reported here.

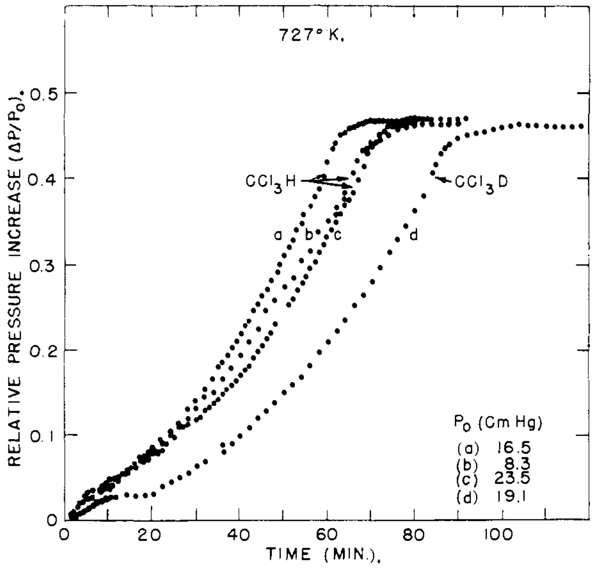

Fig. 1.—Pressure rise studies in static system.

## Results and Discussion

**A. Static System.**—Figure 1 shows typical results of pressure-rise experiments carried out in the static system at 727 ± 2°K. The time for 25% pressure increase, "$t_{25}$," (very nearly equal to the half-time) showed no trend with initial pressure of chloroform. For five experiments with $P_0(\mathrm{CCl_3H})$ in the range 8–26 cm. $t_{25}$ was 48 ± 2 min. This may be compared with the value $t_{25} = 24$ min. at 725°K. from the experiment of Verhoek.[3] Graphical differentiation of pressure-rise–time curves gave initial rates of about $3.5 \times 10^{-3}$ min.$^{-1}$ which remained approximately first order in chloroform, in accord with Verhoek.[3]

For chloroform-*d*, the value of $t_{25}$ was 66 min.; the average initial rate was about $2.5 \times 10^{-3}$ min.$^{-1}$. More precise experiments using the flow system (as reported below) offered a much more reliable determination of the deuterium effect on the rate.

The reaction was found to be inhibited by hydrogen chloride. At 727°K., HCl ($P_0 = 7.4$ cm.) was added to $\mathrm{CCl_3H}$ ($P_0 = 21.1$ cm.); the resulting value of $t_{25}$ was 75 min. Similar inhibition due to HCl was observed in the case of chloroform-*d*. The rate of pressure rise was, however, accelerated by added tetrachloroethylene (the major organic product), as discussed in Part I. For a run at 727°K. in which $\mathrm{C_2Cl_4}$ (2.8 cm.) was added to $\mathrm{CCl_3H}$ (16.6 cm.), $t_{25}$ was 10 min.

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(1) (a) Part of a Ph.D. dissertation submitted by G.P.S. to the Graduate School of Illinois Institute of Technology; (b) Electrochemical Laboratories, Tulsa, Okla.

(2) G. P. Semeluk and R. B. Bernstein, This Journal, **76**, 3793 (1954).

(3) F. H. Verhoek, *Trans. Faraday Soc.*, **31**, 1525 (1935).

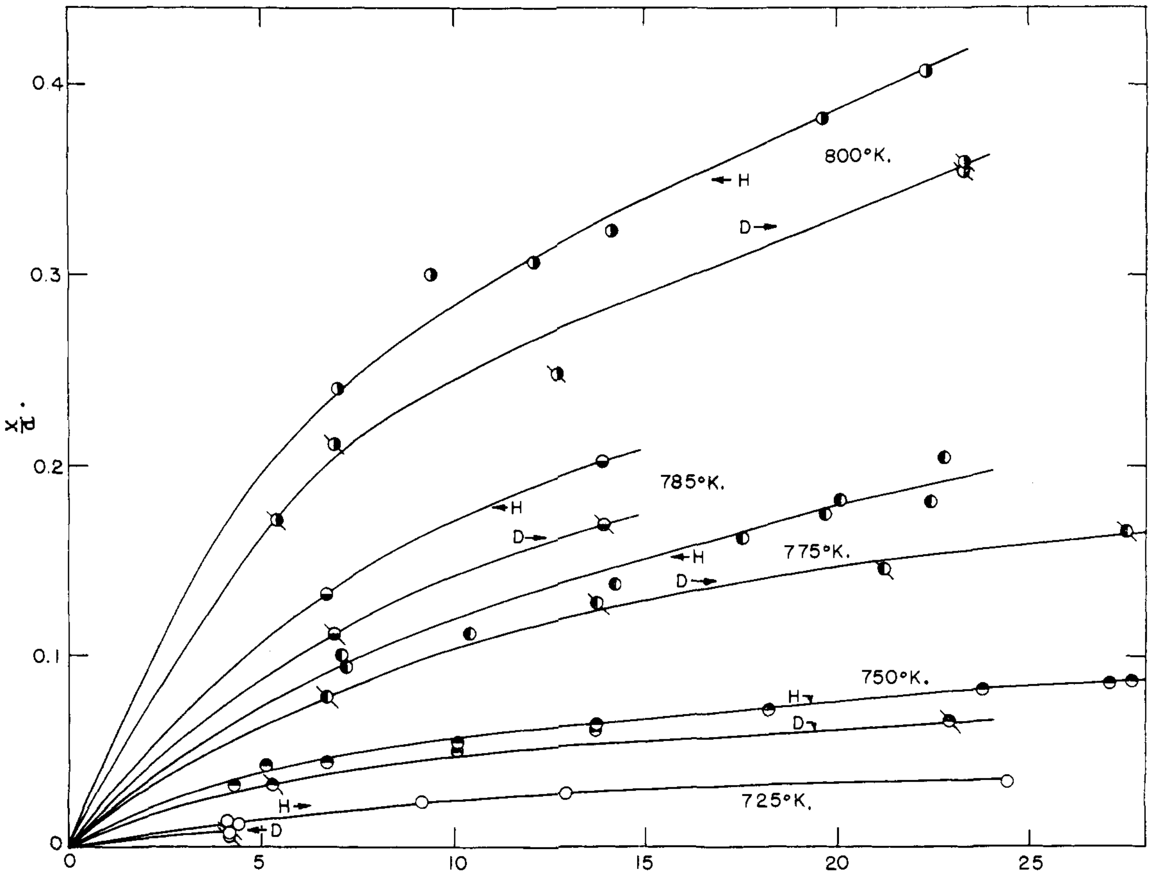

Fig. 2.—Kinetic data for pyrolysis of $CCl_3H$ and $CCl_3D$ in flow system.

**B. Flow System.**—Using the flow system (described in Part I) it was possible to study the reaction in considerably greater detail. For most of the experiments it was customary to carry out a complete material balance; the results were usually better than 97%. The data are expressed in terms of $x/a$, the fraction of HCl produced, and $x_i/a$, the fraction of the various organic products ($i = 1, .., 6$) formed in the run.

Table I lists results of several experiments at 775°K. showing the small effect of chloroform concentration upon the rate (as measured by HCl formation), which indicates that the reaction is first order in chloroform.

TABLE I

INFLUENCE OF CHLOROFORM INPUT CONCENTRATION ON $x/a$

| $[CCl_3H]_0$ (mole/l.) | $t_c$ (sec.) | $x/a$ |
|---|---|---|
| $1.21 \times 10^{-4}$ | 20.1 | 0.183 |
| $4.73 \times 10^{-4}$ | 19.7 | .175 |
| $1.07 \times 10^{-3}$ | 22.4 | .181 |
| | Av. | $0.180 \pm 0.003$ |

Figure 2 shows the fraction of HCl (or DCl) produced, $x/a$, *versus* contact time, $t_c$. The mole fraction of chloroform in the helium carrier was less than 0.07 in all experiments.

Figure 3 shows the fraction of the various organic products formed, $x_i/a$, *versus* $x/a$ at the different temperatures. The dashed line represents the stoichiometric equation observed[2] for complete decomposition: $2CCl_3H \rightarrow 2HCl + C_2Cl_4$; it is, of course not expected to be applicable at low extent of reaction.

Figure 4 is a plot of the fraction of chloroform

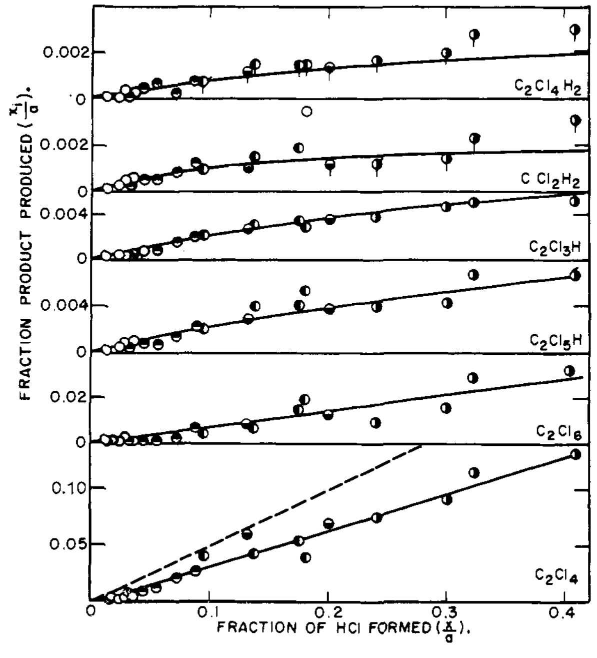

Fig. 3.

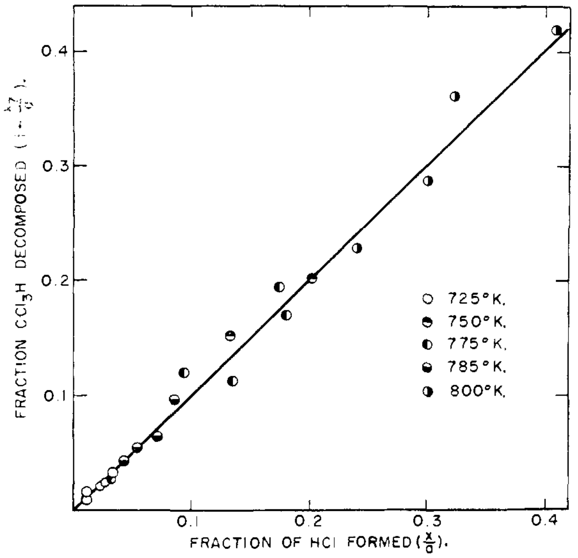

Fig. 4.

decomposed, $(1 - x_7/a)$, determined by infrared analysis, *versus* $x/a$, for all flow experiments in which complete analyses of products were carried out. The line drawn has a slope of unity. Thus the fraction of substrate decomposed is approximately equal to the fraction of HCl produced; since the latter quantity may be determined with good precision it has been taken as the measure of the extent of reaction.

For low chloroform concentrations it may easily be shown that the initial slopes of the plots of $x/a$ *vs.* $t_c$ are equal to the initial rate constants. These values, obtained graphically from large-scale plots of the data of Fig. 2, are listed in Table II. The estimated uncertainty in the rate constants is ±10%.

TABLE II

INITIAL RATE CONSTANT AND ISOTOPE EFFECT FOR THE PYROLYSIS OF $CCl_3H$ AND $CCl_3D$

| $T$ (°K.) | $k_H$ (sec.$^{-1}$) | $k_D$ (sec.$^{-1}$) | $k_H/k_D$ |
|---|---|---|---|
| 725 | $3.66 \times 10^{-3}$ | $2.90 \times 10^{-3}$ | 1.26 |
| 750 | $1.01 \times 10^{-2}$ | $8.30 \times 10^{-3}$ | 1.22 |
| 775 | $1.84 \times 10^{-2}$ | $1.54 \times 10^{-2}$ | 1.19 |
| 785 | $2.52 \times 10^{-2}$ | $2.00 \times 10^{-2}$ | 1.26 |
| 800 | $4.56 \times 10^{-2}$ | $3.80 \times 10^{-2}$ | 1.20 |

The least-squares values of the activation energies are 37.2 ± 2.0 and 37.5 ± 2.0 kcal./mole for chloroform and chloroform-*d*, respectively; the frequency factor is $6.3 \times 10^8$ sec.$^{-1}$ in both cases. Verhoek[3] estimated the activation energy to be 49 kcal./mole.

As a check on the experimental value of the isotope effect two flow experiments were carried out at 800°K. using the competitive method. A feed mixture of 49.2% $CCl_3D$ in $CCl_3H$ was used. For $t_c$ = 23.7 and 38.1 sec., the ratio of HCl to DCl produced[4] was 1.17 ± 0.03 and 1.20 ± 0.03, respectively, in good agreement with the value of $k_H/k_D$ = 1.20 from Table II.

It is difficult to make a precise comparison between the results of the static and flow experiments. As an approximation (based on the stoichiometry for complete decomposition)

$$r = \frac{d(x/a)}{dt_c} = 2\left(\frac{dP/P_0}{dt}\right)$$

where the left side represents the average rate in the flow run and the right side is twice the average rate of relative pressure rise in the static run. At 725°K., from the two points at the greatest contact times one obtains $r = 3.2 \times 10^{-2}$ min.$^{-1}$ at $t_c = 0.32$ min., $r$ decreasing with $t_c$. For the most nearly comparable static runs the earliest measurable values were in the range $0.7 \times 10^{-2}$ to $1.8 \times 10^{-2}$ min.$^{-1}$ at $t = 3$ min. Thus the two sets of experiments are concordant in so far as comparison is possible.

The surface-to-volume ratio for the flow reactor was 19 cm.$^{-1}$ compared to 1.3 cm.$^{-1}$ for the static reactor. The small effect of this difference in the surface–volume ratio, and the reproducibility of all rate measurements after carbonizing the reactors suggest that the decomposition was homogeneous under the conditions of these experiments.

From the curves of Fig. 2 it is seen that the reaction is product-inhibited; the rate law is of the form

$$-\frac{d}{dt}[CCl_3H] = k[CCl_3H]/f(C)$$

where $f(C)$ is a function of the concentration of some product, presumably HCl. The inhibition function which best represents the data is $f(C) = (1 + bC)^{1/2}$.

Thus a plot of $\{f(C)\}^2 - 1$ *versus* $C$ should be linear through the origin. Figure 5 shows several such graphs[5] indicating that the rate equation at low extent of reaction is

$$-\frac{d}{dt}[CCl_3H] = k[CCl_3H]/(1 + b[HCl])^{1/2}$$

The mechanism proposed is

$$CCl_3H \longrightarrow CCl_2H\cdot + Cl\cdot \qquad (1)$$

$$Cl\cdot + CCl_3H \rightleftarrows HCl + CCl_3\cdot \qquad (2)$$

$$CCl_3\cdot + Cl\cdot \longrightarrow CCl_4 \qquad (3)$$

$$CCl_3\cdot \longrightarrow CCl_2\colon + Cl\cdot \qquad (4)$$

$$CCl_2\colon + CCl_3H \longrightarrow C_2Cl_4 + HCl \qquad (5)$$

One obtains by use of the steady-state assumption the experimental rate expression above, with $k = (2k_1k_2k_4/k_3)^{1/2}$ and $b = k_{-2}/k_4$. The isotope effect for the initial rate is thus

$$k_H/k_D = (k_{1H}\,k_{2H}/k_{1D}\,k_{2D})^{1/2}$$

Newton and Rollefson[6] measured the relative rates of photochlorination of $CCl_3H$ and $CCl_3D$ from 253–453°K. Extrapolation of their results to 750°K. gives $k_{2H}/k_{2D}$ = 2.26, subject to considerable uncertainty. The ratio $k_{1H}/k_{1D}$ may be estimated to be about 1.05 using the method of Bigel-

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(4) Infrared analyses of mixtures of HCl and DCl were based on the absorbancies of the P and R branch maxima for each molecule. Effects of pressure broadening were minimized, and the method was checked with known mixtures of similar composition at similar pressures.

(5) To evaluate $f(C)$, the slopes $S$ of the smooth curves of Fig. 2 were measured at several points, then $f(C) = k(1 - x/a)/S$, where $k$ is the initial slope. The determination of the inhibition constant $b$ is subject to large errors; any apparent temperature dependence of $b$ is quite unreliable.

(6) T. W. Newton and G. K. Rollefson, *J. Chem. Phys.*, **17**, 718 (1949).

eisen,[7] with the assumption of the "rigid" model for the activated complex. The resulting calculated ratio $k_H/k_D = 1.54$ does not agree well with the observed value of 1.22. The discrepancy has not been resolved.

The proposed mechanism indicates that $E_H = (E_1 + E_2 + E_4 - E_3)/2 = 37.2$ kcal./mole. Taking $E_2 = 8$ kcal./mole,[8] and estimating $E_3 = 6$ kcal./mole (approximately the activation energy for recombination of $CCl_3$ radicals),[9] then[10] $E_1 = 72 - E_4$; thus the upper limit for the C–Cl bond dissociation energy in chloroform is 72 kcal./mole. It is of interest to note that Sullivan and Davidson[11] give a value for the C–Cl bond dissociation energy in $CCl_4$ in the range 68–75 kcal./mole.

A number of other mechanisms were considered; these included primary fission of the C–H bond,[12] intramolecular elimination of HCl, etc., but none yielded the observed rate expression or a calculated isotope effect of a reasonable order of magnitude. The proposed mechanism appears to be the simplest one which explains the main features of the kinetics; unfortunately, even in the initial stages of the decomposition it is inadequate in some details.[13] The over-all reaction is evidently very complex and a complete quantitative treatment appears unlikely.

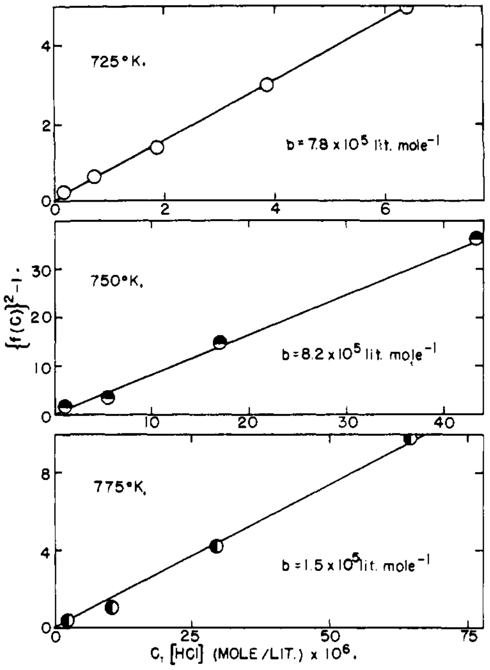

Fig. 5.—Inhibition function *vs.* [HCl].

**Acknowledgments.**—Support of this work by the U. S. Atomic Energy Commission is gratefully acknowledged. The authors are indebted to Drs. H. E. Gunning, G. Gavlin, S. I. Miller, W. H. Urry and K. E. Howlett for helpful comments.

ANN ARBOR, MICHIGAN

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(7) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(8) H. J. Schumacher, *Angew. Chem.*, **53**, 501 (1940).

(9) See the review article by Burnett and Melville, *Chem. Rev.*, **54**, 283 (1954).

(10) From the inhibition plots in Fig. 5, $b = k_{-2}/k_4 \cong 10^6$ l. mole$^{-1}$ at 750°K. $\Delta H_2$ is estimated to be about 12 kcal./mole (from thermochemical data), so $E_{-2} \cong 20$ kcal./mole. Thus $k_2/k_4 >> 10^6$ and it is probable that $E_4 \geq E_2$.

(11) J. H. Sullivan and N. Davidson, *J. Chem. Phys.*, **19**, 143 (1951).

(12) The C–H bond dissociation energy $CCl_3H$ is estimated[10] to lie in the range 89–96 kcal./mole, which is appreciably greater than the highest reasonable value for the C–Cl energy. For a mechanism involving primary C–H bond fission, assuming the "rigid" model for the activated complex, a calculated value of $k_{1H}/k_{1D} = 2.12$ at 750°K. was obtained.

(13) NOTE ADDED IN PROOF: Howlett (private communication) suggests that for decomposition reactions of small molecules in the low pressure range bimolecular steps are more probable. Thus in reactions (1), (3) and (4), another species, "M," would appear. The remitting rate law would be

$$-\frac{d}{dt}[CCl_3H] = \frac{k[M]CCl_3H]}{([M] + b[HCl])^{1/2}}$$

For the flow runs M = He, and the rate law is indistinguishable from that observed; for the static runs M = $CHCl_3$, and the resulting 3/2 order expression for the initial rate would not agree with the approximate 1st order behavior observed (*cf.* Section A).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

# The Mole Ratio Method for Spectrophotometric Determination of Complexes in Solution[1]

BY ALBERT S. MEYER, JR., AND GILBERT H. AYRES

RECEIVED JUNE 7, 1956

A mathematical treatment is given of the mole ratio method for deducing the stoichiometry of complexes in solution, for situations in which several complexes exist under a given set of experimental conditions. For the ideal case, the absorbance of the solutions as a function of concentration of variable component is a continuous curve made up of straight line segments. Changes of slope may be observed at any mole ratio of one of the complexes formed, except for very unusual relations between absorptivities, at restricted wave lengths, of adjacent complexes. The stoichiometry of all the complexes in solution can be defined by spectrophotometric measurements of solutions of mole ratios corresponding to each complex, of one solution between successive complexes, and of two solutions above and two solutions below the mole ratio of the terminal complexes, provided measurements are made at sufficient different wave lengths. The absence of a change of slope, in the mole ratio plot, over the entire spectrum is strong evidence that a complex of a given mole ratio does not exist. Consideration of the effects of dissociation of the complexes and the tolerances in the reliability of the spectrophotometric measurements leads to the conclusion that the minimum ratio between successive stepwise dissociation constants must be 600 to permit extrapolation of linear portions of absorbance *versus* mole ratio plots to their intersection point as representing the composition of a complex. The advantages of the mole ratio method over the method of continuous variations are discussed.

The mole ratio method of deducing the composition of complexes in solution from spectrophotometric data was introduced by Yoe and Jones.[2]

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[1] This work was supported jointly by The United States Atomic Energy Commission and The University of Texas, under Contract No. AT-(40-1)-1037.

[2] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 11 (1944).