Investigation of the Composition and Formation Constant of Molecular Complexes

(Job method/nuclear magnetic resonance)

R. SAHAI*, G. L. LOPER*†, S. H. LIN*, AND H. EYRING†

* Department of Chemistry, Arizona State University, Tempe, Ariz. 85281; and † Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Contributed by Henry Eyring, December 17, 1973

ABSTRACT It has been the purpose of the present paper to investigate and explore the conditions under which the linear relation between Δ/C_D^0 and Δ in the Hanna-Ashbaugh-Foster-Fyfe equation for the evaluation of equilibrium constants holds, (C_D^0 is initial concentration of a donor and Δ is the observed chemical shift relative to the chemical shift of the acceptor) to obtain the equation representing the exact linear relation between Δ/C_D^0 and Δ , when the linear relation between Δ/C_D^0 and Δ holds, and to discuss how to use the Job method in nuclear magnetic resonance measurements to determine the stoichiometry of molecular complexes. We have found that the conventional belief that C_D^0 should always be chosen to be much greater than C_A^0 (initial concentration of acceptor) is not necessarily always true and the exact linear relation between Δ/C_D^0 and Δ is represented by the equation $\Delta/C_D^0 = K_1\Delta/(1 + K_1C_A^0) - K_1\Delta/(1 + K_1C_A^0)^2$, where K_1 is the formation constant of the complex. It is shown that in the Job method of nuclear magnetic resonance measurements one has to plot ΔC_A^0 against the mole fraction, and the mole fraction at the maximum should give us the composition of the complex. Theoretical results have been verified experimentally on the weak interaction between naphthalene and methyl iodide.

There has been an upsurge of research interest in molecular complexes of the donor-acceptor type during the last two decades (1). Despite the large number of papers dealing with molecular complexes, only a small percentage of these studies use nuclear magnetic resonance (NMR) spectroscopy as a means of determining complex formation equilibria, their compositions, and thermodynamic data. More recent papers include the work of Kuntz (2, 3), Foster (4, 5), Hanna (6, 7), and their coworkers. In particular, Hanna and Ashbaugh (6), observing the basic assumption of Huggins and Pimentel (8) for the correlation of the NMR measurements to the equilibrium, noted that equilibrium constants in hydrogen-bonding systems can successfully be determined by NMR spectroscopy (9), and that complex formation equilibria between donors and acceptors are similar to those found in hydrogen-bonding systems. According to Hanna and Foster, if the concentration of acceptor is kept considerably lower than that of the donor, then the plot of the ratio of the observed chemical shift relative to the chemical shift of the acceptor to the donor concentration, Δ/C_D^0 , against the observed chemical shift

relative to the chemical shift of the acceptor, Δ , is linear,

$$\Delta/C_D^0 = K_1(\Delta_0 - \Delta) \quad [1]$$

where Δ_0 represents the chemical shift of the molecular complex relative to the chemical shift of the acceptor and K_1 , the complex formation constant. From Eq. 1 one can determine K_1 . The question now arises: even if the plot of Δ/C_D^0 versus Δ is linear, does Eq. 1 really represent the exact linear relationship? It has been the purpose of this paper to investigate the conditions under which the linear relation between Δ/C_D^0 and Δ holds, to obtain the equation representing the exact linear relation between Δ/C_D^0 and Δ when the linear relation between Δ/C_D^0 and Δ holds, and to discuss how to use the Job method by using NMR measurements. The theoretical results have been verified experimentally on the weak interactions between aromatic hydrocarbon and alkyl halides.

Theoretical results obtained in this paper, of course, can be applied not only to molecular complexes but also to hydrogen-bonding systems.

THEORETICAL

(a) 1:1 Complexes

Considering the equilibrium for 1:1 complexes, we have

and

$$K_1 = \frac{C_{AD}}{(C_A^0 - C_{AD})(C_D^0 - C_{AD})} \quad [3]$$

where C_A^0 and C_D^0 represent the initial concentrations of A (acceptor) and D (donor), respectively, and C_{AD} is the equilibrium concentration of the complex. γ_i in Eq. 2 is the Raoult activity coefficient of species i . In general, K_1 and K_γ are not constant but are functions of concentrations of reactants and products. In this investigation, as we are concerned with the discussion of the limitation of the Hanna-Ashbaugh-Foster-Fyfe (HAFF) equation 1, as with Hanna and Foster, we shall assume that K_1 and K_γ are constant. This assumption will, however, be investigated in a later paper. Since in most NMR measurements, we keep C_A^0 constant and vary C_D^0 , it is convenient to define a set of dimensionless quantities as follows: $K_1^* = K_1 C_A^0$; $C_D^{0*} = C_D^0/C_A^0$; $C_{AD}^* = C_{AD}/C_A^0$. In terms of these dimensionless quantities, Eq. 3 becomes,

$$K_1^* = \frac{C_{AD}^*}{(1 - C_{AD}^*)(C_D^{0*} - C_{AD}^*)} \quad [4]$$

Abbreviations: NMR, nuclear magnetic resonance; HAFF equation, Hanna-Ashbaugh-Foster-Fyfe equation.

† Permanent address: Department of Chemistry, University of California, Irvine, Calif. 92664.

FIG. 1. Theoretical relationship between C_{DA}^* ($= \Delta^*$) and C_D^{0*} for different K_1^* .

Solving for C_{AD}^* from Eq. 4 yields,

$$C_{AD}^* = \frac{1}{2} \left(1 + C_D^{0*} + \frac{1}{K_1^*} \right) - \frac{1}{2} \left[\left(1 + C_D^{0*} + \frac{1}{K_1^*} \right)^2 - 4C_D^{0*} \right]^{1/2} = \sum_{k=1}^{\infty} \frac{(2k-2)!}{k! \cdot (k-1)!} \frac{C_D^{0*k}}{(1 + C_D^{0*} + 1/K_1^*)^{2k-1}} = \frac{C_D^{0*}}{1 + C_D^{0*} + 1/K_1^*} \left[1 + \frac{C_D^{0*}}{(1 + C_D^{0*} + 1/K_1^*)^2} + \dots \right] \quad [5]$$

by applying the binomial expansion. Eq. 5 indicates that when $C_D^{0*} \ll 1/K_1^*$, C_{AD}^* varies linearly with C_D^{0*} . Fig. 1 shows the theoretical plots between C_{DA}^* and C_D^{0*} for different K_1^* values. These plots indicate that the linear relation between C_{DA}^* and C_D^{0*} holds only up to $K_1^* = 10^{-2}$.

Now, in the NMR measurements it is assumed that the free and complexed forms of the acceptor each has characteristic precessional frequencies (ν_A and ν_{AD} , respectively) and that the observed resonance frequency (ν_{obsd}) is the weighted arithmetic mean (8),

$$\nu_{\text{obsd}} = \left(\frac{C_A^0 - C_{AD}}{C_A^0} \right) \nu_A + \frac{C_{AD}}{C_A^0} \nu_{AD} = (1 - C_{AD}^*) \nu_A + C_{AD}^* \nu_{AD} \quad [6]$$

or

$$\nu_{\text{obsd}} - \nu_A = C_{AD}^* (\nu_{AD} - \nu_A); C_{AD}^* = \Delta / \Delta_0 = \Delta^* \quad [7]$$

where $\Delta = \nu_{\text{obsd}} - \nu_A$, and $\Delta_0 = \nu_{AD} - \nu_A$. Eq. 7 indicates that C_{AD}^* is proportional to Δ^* . Thus if we prepare a theoretical plot of $\log \Delta^*$ (or $\log C_{AD}^*$) versus $\log C_D^{0*}$ for various K_1^* , then by superimposing an experimental plot of $\log \Delta$ versus $\log C_D^0$ we can determine K_1^* and hence K_1 . From Eq. 7 we can see that Δ is always smaller than Δ_0 . Substitution of

FIG. 2. Theoretical plots of Δ^*/C_D^{0*} against Δ^* for different K_1^* .

Eq. 7 into Eq. 4 gives

$$K_1^* = \frac{\Delta^*}{(1 - \Delta^*)(C_D^{0*} - \Delta^*)} = \frac{\Delta^*/C_D^{0*}}{(1 - \Delta^*)(1 - \Delta^*/C_D^{0*})} \quad [8]$$

If we choose $C_D^{0*} \gg 1$ ($C_D^0 \gg C_A^0$), then $\Delta^*/C_D^{0*} \ll 1$, and Eq. 8 reduces to the Hanna-Ashbaugh (6)-Foster-Fyfe equation (4)

$$\Delta^*/C_D^{0*} = K_1^* (1 - \Delta^*) \quad [9]$$

after neglecting Δ^*/C_D^{0*} compared with unity. Eq. 9 or Eq. 1 indicates that a plot of Δ/C_D^0 versus Δ is linear and from the slope of this straight line one can determine K_1 and from the intercept, Δ_0 . To find the exact linear relation between Δ^*/C_D^{0*} and Δ^* , we rewrite Eq. 8 as

$$\Delta^*/C_D^{0*} = \frac{K_1^* (1 - \Delta^*)}{(1 + K_1^*) [1 - (K_1^* \Delta^*/1 + K_1^*)]} = Y_1(\Delta^*) \quad [10]$$

and expand $Y_1(\Delta^*)$ in terms of Δ^* by Taylor's expansion (10),

$$\Delta^*/C_D^{0*} = \frac{K_1^*}{1 + K_1^*} - \frac{K_1^*}{(1 + K_1^*)^2} \Delta^* + R_1(\Delta^*) \quad [11]$$

where

$$R_1(\Delta^*) = - \frac{1}{1 + K_1^* - K_1^* \Delta^*} \left(\frac{K_1^* \Delta^*}{1 + K_1^*} \right)^2 \quad [12]$$

$R_1(\Delta^*)$ represents the higher order correction terms. It should be noticed that Eq. 11 reduces to Eq. 9 only when $K_1^* \ll 1$. From the above derivation, we can see that the linear equation given by Eq. 11 represents the tangential line of the curve Δ^*/C_D^{0*} versus Δ^* at $\Delta^* = 0$.

From Eq. 10 we can see that the second term of Eq. 10 does not involve C_D^{0*} explicitly and that the linear relation between Δ^*/C_D^{0*} and Δ^* is determined by K_1^* . In other

words, as long as we can keep K_1^* (the product of the equilibrium constant and the initial concentration of acceptor A) small enough so that $(K_1^*\Delta^*/1 + K_1^*)^2$ is within the experimental accuracy small compared with unity, we may expect a good linear relation between Δ^*/C_D^{0*} and Δ^* to hold regardless of what donor concentration we use. Fig. 2 shows the theoretical relation between Δ^*/C_D^{0*} and Δ^* for different K_1^* values. An analysis of these plots indicates that the linear relation between Δ^*/C_D^{0*} and Δ^* holds only up to K_1^* about 0.2 and above this, it starts deviating from linearity.

To compare the best linear relation Δ^*/C_D^{0*} versus Δ^* , with the conventional linear relation between Δ^*/C_D^{0*} and Δ^* , we write Eq. 9 as

$$\Delta^*/C_D^{0*} = K_1^* (1 - \Delta^*) + R_{1H}(\Delta^*) \quad [11a]$$

where the correction term $R_{1H}(\Delta^*)$ is given by

$$R_{1H}(\Delta^*) = -K_1^*(1 - \Delta^*) \Delta^*/C_D^{0*}, \quad \text{or} \quad \frac{R_{1H}(\Delta^*)}{\Delta^*/C_D^{0*}} = -K_1^*(1 - \Delta^*) \quad [13]$$

which should be compared with

$$\frac{R_1(\Delta^*)}{\Delta^*/C_D^{0*}} = -\frac{K_1^*}{1 - \Delta^*} \left(\frac{\Delta^*}{1 + K_1^*} \right)^2 \quad [14]$$

From Eqs. 13 and 14 we can determine the errors introduced by the HAFF equation and the exact linear relation.

It can easily be shown that the linear equation given by Eq. 11a actually represents the tangential line of the curve of Δ^*/C_D^{0*} versus Δ^* at $\Delta^* = 1$, if we notice that $Y_1'(1) = -K_1^*$, and Δ^*/C_D^{0*} equals zero at $\Delta^* = 1$. A theoretical comparison of the relation between Δ^*/C_D^{0*} and Δ^* generated by Eqs. 9, 10, and 11 for different K_1^* values is shown in Fig. 3. It may be seen from this figure that the HAFF equation and the exact linear relation are almost the same and in good agreement with the exact theoretical one only when K_1^* is smaller than 0.1. As K_1^* increases, both plots deviate from the exact theoretical plot, and it can be noticed that the HAFF Eq. 11a represents the tangential line of the curve Δ^*/C_D^{0*} versus Δ^* , at $\Delta^* = 1$, and Eq. 11 represents the tangential line of Δ^*/C_D^{0*} versus Δ^* , at $\Delta^* = 0$ as shown above.

(b) 1:n Complexes

We realize that in molecular complexes when the 1:n complex is formed, it usually is accompanied by the formation of 1:1, 1:2...1:n-1 complexes. The reason that we discuss the NMR determination of 1:n complexes ignoring the existence of 1:1, 1:2, ..., 1:n-1 complexes here is that we hope that the derivation given here may be found useful in areas other than ordinary molecular complexes, and that the derived results for 1:n complexes will be used in the discussion of the Job method by the NMR measurement. The multiple equilibria will be discussed in a later paper.

In this case, we have,

$$A + nD \xrightleftharpoons{K_n} AD_n \quad (n > 1) \quad [15]$$

and

$$K_n = \frac{C_{AD_n}}{C_A C_D^n} = \frac{C_{AD_n}}{(C_A^0 - C_{AD_n})(C_D^0 - nC_{AD_n})^n} \quad [16]$$

In reality the activity rather than the concentration should

FIG. 3. Comparison of theoretical relationship between Δ^*/C_D^{0*} and Δ^* for different K_1^* using different derivations. Continuous line—exact equation; broken line—Foster-Fyfe equation; dotted line—our equation.

be used in Eq. 16. In terms of dimensionless quantities defined by

$$K_n^* = K_n C_A^{0n}; C_{AD_n}^* = C_{AD_n}/C_A^0; C_D^{0*} = C_D^0/C_A^0 \quad [17]$$

Eq. 16 becomes

$$K_n^* = \frac{C_{AD_n}^*}{(1 - C_{AD_n}^*)(C_D^{0*} - nC_{AD_n}^*)^n} \quad [18]$$

Introducing the relation $C_{AD_n}^* = \Delta/\Delta_0 = \Delta^*$, given in Eq. 7, into the Eq. 18, we obtain

$$K_n^* = \frac{\Delta^*}{(1 - \Delta^*)(C_D^{0*} - n\Delta^*)^n} = \frac{\Delta^*/C_D^{0*n}}{(1 - \Delta^*)(1 - n\Delta^*/C_D^{0*})^n} \quad [19]$$

If we can choose the condition so that $n\Delta^*/C_D^{0*} \ll 1$, then Eq. 19 becomes

$$\Delta^*/C_D^{0*n} = K_n^* (1 - \Delta^*) \quad [20]$$

which indicates that Δ^*/C_D^{0*n} versus Δ^* is linear. To obtain the exact linear relation between Δ^*/C_D^{0*n} and Δ^* , we let $\Delta^*/C_D^{0*n} = Y_n(\Delta^*)$. Solving for $Y_n(\Delta^*)$, we obtain (10)

$$Y_n(\Delta^*) = \frac{\Delta^*}{C_D^{0*n}} = \frac{K_n^*(1 - \Delta^*)}{(1 + n\Delta^*[K_n^*(1/\Delta^* - 1)]^{1/n})^n} \quad [21]$$

Now, applying the binomial expansion to Eq. 21, we obtain (10) (I) for $n \neq 1, 2$

$$\Delta^*/C_D^{0*n} = K_n^* (1 - \Delta^*) + R_n(\Delta^*) \quad [22]$$

where

$$R_n(\Delta^*) = K_n^* (1 - \Delta^*) \times \left[\left(1 + n\Delta^* \left[K_n^* \left(\frac{1}{\Delta^*} - 1 \right) \right]^{1/n} \right)^{-1} - 1 \right] \quad [23]$$

FIG. 4. A typical set of experimental results showing the plot of Δ/C_D^0 against Δ , in cycles per second, for the interaction of naphthalene with methyl iodide in carbon tetrachloride at 10°C.

and (II) for $n = 2$,

$$\Delta^*/C_D^{0*2} = K_2^* - K_2^*\Delta^* (1 - 12 K_2^*) + R_2(\Delta^*) \quad [24]$$

where

$$R_2(\Delta^*) = -12 K_2^{*2} \Delta^* + K_2^*(1 - \Delta^*) \times \left[\left(1 + 2\Delta^* \left[K_2^* \left(\frac{1}{\Delta^*} - 1 \right) \right]^{1/2} \right)^{-1} - 1 \right] \quad [25]$$

From the above derivation, we can see that the mere fact that the plot of Δ^*/C_D^{0*} versus Δ^* is linear already suggests that the complex is of the 1:1 type, provided that the deviation from ideality is negligible.

(c) The Job method in NMR measurements

Now, we consider the application of the Job method in NMR measurements to determine the composition of molecular complexes. For this purpose we consider 1: n complexes as given in Eq. 15. This is consistent with the discussion of the Job method in other measurements (11). Again the deviation from ideality is neglected. Let us assume, V_A and V_D are the volumes of A and D, respectively, and $V = V_A + V_D$. Then the total concentration C_T is given by

$$C_T = 1/V(V_A C_A^i + V_D C_D^i) = 1/V[(V - V_D) C_A^i + V_D C_D^i] \quad [26]$$

where C_A^i and C_D^i represent the concentration of the stock solutions of A and D, respectively. From Eq. 16, we have

$$C_{AD_n} = K_n(C_A^0 - C_{AD_n})(C_D^0 - nC_{AD_n})^n = K_n[(1 - V_D/V) C_A^i - C_{AD_n}] \times [V_D/V C_D^i - nC_{AD_n}]^n \quad [27]$$

Let $V_D/V = v$ and $C_D^i/C_A^i = r$. Then

$$C_{AD_n} = K_n[(1 - v)C_A^i - C_{AD_n}](vC_A^i r - nC_{AD_n})^n \quad [28]$$

To find the maximum value of C_{AD_n} by varying v , we calcu-

FIG. 5. A typical set of experimental results on Job method showing the plot of ΔC_A^0 against X_D for the determination of the stoichiometry of the complex ($C_{10}H_8:CH_3I$).

late

$$\frac{1}{C_{AD_n}} \cdot \frac{\partial C_{AD_n}}{\partial v} = \frac{-C_A^i - \partial C_{AD_n}/\partial v}{(1 - v)C_A^i - C_{AD_n}} + n \frac{rC_A^i - n\partial C_{AD_n}/\partial v}{vrC_A^i - nC_{AD_n}} \quad [29]$$

Setting $\partial C_{AD_n}/\partial v = 0$, we obtain

$$C_{AD_n} n(r - 1) = rC_A^i [v - n(1 - v)] \quad [30]$$

If we choose $r = 1$, then

$$v = \frac{n}{1 + n}; C_T = C_A^i = C_D^i \quad [31]$$

But $C_{AD_n}/C_A^0 = \Delta/\Delta^0$ or $C_{AD_n} = \Delta/\Delta^0 C_A^0$. Therefore, if C_{AD_n} is a maximum, then $\Delta/\Delta^0 C_A^0$ would also be a maximum at $v = n/1 + n$. Thus by plotting ΔC_A^0 (or $\Delta/\Delta^0 C_A^0$) against X_D (mole fraction of donor), the maximum will occur at $X_D = n/1 + n$. At this point we have

$$K_n = \frac{\Delta/\Delta_0}{(C_D^0)^n (1 - \Delta/\Delta_0)^{n+1}} \quad [32]$$

where $C_D^0 = X_D C_T = n/1 + n C_T$. Eq. 32 can also be used to determine the equilibrium constant K_n after determining n . The work in progress is a study of the Job method in NMR measurements for the multiple equilibria.

EXPERIMENTAL

The materials used in the present investigation, and the procedure of experimentation were essentially the same as reported elsewhere (12). Solutions were prepared by dissolving varying amounts of naphthalene (0.2–2.0 M) and a constant amount of methyl iodide (1.0 M) in carbon tetrachloride. We realize that CCl_4 probably is not a good choice as a solvent for aromatic molecules. In this preliminary communication, we just want to demonstrate the theoretical results we obtained. For the Job method the solutions were prepared by

mixing x ml of 2.0 M naphthalene with $(10 - x)$ ml of 2.0 M methyl iodide solution, both in carbon tetrachloride (where x was varied from 0 to 10 ml and the total volume was kept at 10 ml). Nuclear magnetic resonance spectra were taken on a Varian Associate A-60 spectrometer operating at 60 MHz and equipped with a Varian temperature controller. Line positions of the methyl iodide acceptor molecule were measured using an internal cyclohexane resonance reference. Chemical shifts were reproducible to better than 0.3 Hz, the uncertainty being determined by the line width. All measurements were made at 10°C, the temperature of the probe. Shifts in the signal, caused by additions of electron donor to the system, were to higher field values.

It has been indicated in the previous section that whether the linear relation between Δ^*/C_D^{0*} and Δ^* holds or not depends on the magnitude of K_1^* and does not depend on C_D^{0*} and that C_A^0 does not necessarily have to be kept much smaller than C_D^0 . This point has been verified experimentally on the interaction of naphthalene with methyl iodide and a set of experimental results is shown in Fig. 4. The plot of Δ/C_D^0 against Δ gives a good straight line even though the acceptor concentration (1.0 M) used was comparable to the donor concentration (0.2–2.0 M). The equilibrium constant (0.112 ± 0.003 liter. mol⁻¹), calculated from the slope which was computed by the use of a least squares curve fit program, is within the limit of experimental error in agreement with what we observed earlier (12) for this system, when the donor concentration (0.2–2.0 M) used was much greater than the acceptor concentration (0.01 M).

Fig. 5 shows a typical set of experimental results on the Job method using NMR spectroscopy to determine the stoichiometry of the molecular complex ($C_{10}H_8:CH_3I$). As discussed in the previous section, to apply the Job method in NMR measurements we have to determine the variation for the product of Δ and C_A^0 with mole fraction of donor (naphthalene). It may be seen from this figure that the curve exhibits a maximum when $X_D = 0.5$ and hence indicates the molar ratio of naphthalene to methyl iodide is 1:1. This method can also be

applied to study the stoichiometry of hydrogen-bonding systems by NMR spectroscopy.

One of the authors (R.S., a Postdoctoral Fellow) wishes to thank Miss Katie Reimer for technical assistance and Dr. R. H. Hofeldt for some help in computer programming. H.E. wishes to thank Army Research Contract DA-ARO-D-31-124-72-G15 for supporting Publication. The research was supported by the American Chemical Society Petroleum Research Fund and the National Science Foundation. S.H.L. is a John Simon Guggenheim Fellow.

1. Mulliken, R. S. & Person, W. B. (1969) *Molecular Complexes. A Lecture and Reprint Volume* (John Wiley, New York), pp. 81–100; Foster, R. (1969) *Organic Charge-Transfer Complexes* (Academic Press, New York), pp. 150–176; Rose, J. (1967) *Molecular Complexes* (Pergamon Press, London), pp. 28–84; Andrews, L. J. & Keefer, R. (1964) *Molecular Complexes in Organic Chemistry* (Holden-Day, Inc., San Francisco), pp. 78–108; and Briegleb, G. (1961) *Electronen-Donator-Acceptor Komplexe* (Springer-Verlag, Berlin), pp. 64–85.
2. Kuntz, I. D., Jr. & Johnston, M. J., Jr. (1967) *J. Amer. Chem. Soc.*, **89**, 6008–6017.
3. Johnston, M. D., Jr., Gasparro, F. P. & Kuntz, I. D., Jr. (1969) *J. Amer. Chem. Soc.* **91**, 5715–5724.
4. Foster, R. & Fyfe, C. A. (1965) *Trans. Faraday Soc.* **61**, 1626–1631.
5. Foster, R. & Fyfe, C. A. (1966) *Trans. Faraday Soc.* **62**, 1400–1405.
6. Hanna, M. W. & Ashbaugh, A. L. (1964) *J. Phys. Chem.* **68**, 811–816.
7. Sandoval, H. A. & Hanna, M. W. (1966) *J. Phys. Chem.* **70**, 1203–1206.
8. Huggins, C. M. & Pimentel, G. (1955) *J. Chem. Phys.* **23**, 1244–1247.
9. Berkeley, P. J., Jr. & Hanna, M. W. (1963) *J. Phys. Chem.* **67**, 846–849.
10. The detailed derivation may be obtained from the authors upon request.
11. Rossotti, F. J. & Rossotti, H. (1961) *The Determination of Stability Constants* (McGraw-Hill, New York), pp. 47–51.
12. Sahai, R. & Lin, S. H. (1971) *Can. J. Chem.* **49**, 1771–1774; Loper, G. L. (1971) Ph.D. dissertation (Arizona State University).