[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

# Temperature Independent Factor in the Rate Constant Ratio for Isotopic Reactions: Four Center Systems

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The Bigeleisen–Wolfsberg–Slater treatment of reaction coördinate motion is extended to the calculation for planar four-center systems of the temperature independent part of isotopic rate constant ratios. The results for several configuration types are applied to the acidic hydrolysis of urea. Fair agreement with experiment is found for the intramolecular hydrogen transfer mechanism suggested by Shaw and Bordeaux.

## Introduction

A ratio of isotopic rate constants is the product of two factors, one temperature independent, one temperature dependent.[1–4] Assuming that the transmission coefficient is unaffected by isotopic substitution

$$k_1/k_2 = (\text{TIF})(\text{TDF}) = (m_2^*/m_1^*)^{1/2}(f^0/f^*) \quad (1)$$

where the $f$'s are ratios of isotopic partition functions for the normal and activated species, and the term involving the $m^*$'s is the contribution to the isotope effect of the reaction coördinate motion. The identity of the $m^*$'s depends upon the character of the theory applied to the reaction: in the transition state theory, $m^*$ is the effective mass of the activated complex in the direction of the reaction coördinate; where a Pelzer–Slater potential is employed, $m^*$ is the mass coefficient associated with the reaction coördinate according to the expression[5]

$$\frac{1}{m_1^*} = \sum_i^n \frac{1}{m_i}\frac{\partial q_1}{\partial \mathbf{r}_i} \bullet \frac{\partial q_1}{\partial \mathbf{r}_i} \quad (2)$$

where $q_1$ is the reaction coördinate (expressed as an internal coördinate), and $m_i$ and $\mathbf{r}_i$ are the mass and position vector, respectively, of the $i$th particle (in the molecule).

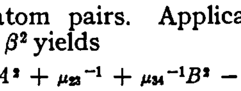
Bigeleisen and Wolfsberg[3,4] have applied eq. 2 to the computation of the TIF in three-center systems involving asymmetric motion with respect to the central atom; Yankwich and Copeland[6] extended the method to include symmetric motion about the central atom, to permit application to isotope fractionation in lead oxalate pyrolysis; Bender and Hoeg[7] applied the method to several nucleophilic substitution reactions of methyl iodide but used the masses of molecular fragments instead of atomic masses.[8] In each of these applications one or more factors operated to complicate the test of the method: in the first work,[3,4] the discussion of examples was not repeated after a sign error was detected; in the lead oxalate system the stoichiometry of the reaction was a function of temperature and the calculations on the observed isotope effect had to be based on assumptions concerning the size of another isotope effect in the reaction; in the work on nucleophilic substitutions each reaction was studied at one temperature only and the use of molecular fragment masses seems to do some violence to our notions concerning the factorizability of secular equations.

In a study of the carbon isotope fractionation in the hydrolysis of urea,[9] Yankwich and Veazie obtained an "experimental" value of TIF by a method[10] which assumed: (i) the applicability of the Redlich–Teller product rule to the activated complexes as well as to the normal molecules,[11] and (ii) the hyperbolic sine representation of vibrational partition functions. Calculated values for TIF were obtained for a three-center representation of the urea molecule, as follows: (i) by assuming the reaction coördinate motion to be a normal vibrational mode with an associated force constant of zero magnitude; (ii) by assuming motion in the reaction coördinate describable by a Bigeleisen–Wolfsberg critical coördinate; (iii) by assuming any of several three-center approximations to the two-center method.[2] In none of these calculations was satisfactory agreement obtained between calculated and "experimental" values of TIF.

In this paper we report the results of an extension of the Bigeleisen–Wolfsberg–Slater approach to planar four-center representations of reacting molecules, with application to urea hydrolysis.

## Planar Four-center Models and Reaction Coördinates

**I. Un-branched Chain, Non-cyclic Coördinate.**—Consider the four-center system



If the 2–3 bond is being broken and the 1–2 and 3–4 bonds formed, the reaction coördinate can be expressed as

$$q = -\alpha|\mathbf{r}_1 - \mathbf{r}_2| + \beta|\mathbf{r}_2 - \mathbf{r}_3| - \gamma|\mathbf{r}_3 - \mathbf{r}_4|$$

where $\alpha$, $\beta$ and $\gamma$ are defined following Bigeleisen and Wolfsberg,[3] and their ratios determine the relative amounts of bond formation and bond rupture between the atom pairs. Application of eq. 2 and division by $\beta^2$ yields

$$(m^*\beta^2)^{-1} = \mu_{12}^{-1}A^2 + \mu_{23}^{-1} + \mu_{34}^{-1}B^2 - \frac{2A}{m_2}\cos\phi_2 - \frac{2B}{m_3}\cos\phi_3 \quad (3)$$

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

(2) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 1952).

(3) J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1972 (1953).

(4) J. Bigeleisen and M. Wolfsberg, *ibid.*, **22**, 1264 (1954).

(5) N. B. Slater, *Proc. Leeds Philosophical Soc.*, **5**, 75 (1949).

(6) P. E. Yankwich and J. L. Copeland, THIS JOURNAL, **79**, 2081 (1957).

(7) M. L. Bender and D. F. Hoeg, *ibid.*, **79**, 5650 (1957).

(8) J. Bigeleisen and M. Wolfsberg, footnote 28 in ref. 7.

(9) P. E. Yankwich and A. E. Veazie, THIS JOURNAL, **80**, 1835 (1958).

(10) P. E. Yankwich and H. S. Weber, *ibid.*, **78**, 564 (1956).

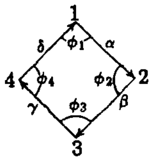
(11) H. S. Johnston, W. A. Bonner and D. J. Wilson, *J. Chem. Phys.*, **26**, 1002 (1957).

where $A = \alpha/\beta$, $B = \gamma/\beta$, and $\mu_{ij}^{-1} = m_i^{-1} + m_j^{-1}$; $A$ and $B$ represent the amounts of bond formation relative to bond rupture.

In cases where the 1–2 and 3–4 bonds are being formed while the middle bond is broken, eq. 3 is obtained, but $A$ and $B$ then measure the amount of bond rupture relative to bond formation. Where a pair of adjacent bonds suffers like fate, the sign of one of the trigonometric terms is reversed and the $A$'s and $B$'s have to be redefined.

The TIF for a pair of isotopic reactions is the square root of the quotient of a pair of equations like (3).

**II. Un-branched Chain, Cyclic Coördinate.**—In metatheses, cyclizations and atom transfer reactions, a convenient general representation is



Unfortunately, introduction of a third parameter like $A$ and $B$ would be required. For simplicity, we show as an example the situation where bonds 2–3 and 4–1 are being ruptured and bonds 1–2 and 3–4 are being formed; further, we set $\gamma = \beta$. This coördinate describes a pseudo intramolecular transfer of atom 3 in a situation where the initial configuration is 4–1–2–3 and the final one is 1–2 + 3–4. Here

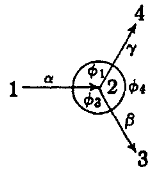
$$q = -\alpha|\mathbf{r}_2 - \mathbf{r}_1| + \beta|\mathbf{r}_3 - \mathbf{r}_2| - \beta|\mathbf{r}_4 - \mathbf{r}_3| + \delta|\mathbf{r}_1 - \mathbf{r}_4|$$

which yields

$$(m^*\delta^2)^{-1} = \mu_{12}^{-1}A^2 + (\mu_{23}^{-1} + \mu_{34}^{-1})B^2 + \mu_{14}^{-1} - 2\left[\frac{A}{m_1}\cos\phi_1 + \frac{AB}{m_2}\cos\phi_2 + \frac{B^2}{m_3}\cos\phi_3 + \frac{B}{m_4}\cos\phi_4\right] \quad (4)$$

where $A = \alpha/\delta$, and $B = \beta/\delta$.

**III. Branched Chain.**—In this case a central atom is attached to the other three



As an example, the rupture of the 2–3 bond while the other two are being formed can be represented by

$$q = -\alpha|\mathbf{r}_2 - \mathbf{r}_1| + \beta|\mathbf{r}_3 - \mathbf{r}_2| - \gamma|\mathbf{r}_4 - \mathbf{r}_2|$$

which yields

$$(m^*\beta^2)^{-1} = \mu_{12}^{-1}A^2 + \mu_{23}^{-1} + \mu_{24}^{-1}B^2 + \frac{2}{m_2}[AB\cos\phi_1 - A\cos\phi_3 - B\cos\phi_4] \quad (5)$$

where $A = \beta/\alpha$, and $B = \gamma/\beta$.

## Application to Urea Hydrolysis

The square root of the quotient of an isotopic pair of relations such as those in eq. 3, 4, and 5 is the TIF for a pair of isotopic reactions in terms of molecular constants and the parameters $A$ and $B$. A convenient representation of such a function is a plot of lines of equal TIF (*isotifs*) on an $A$-$B$ plane, *vide infra.*

The "experimental" value of TIF for the acidic hydrolysis of urea is 1.016 ± 0.002.[9] In Fig. 1 and Fig. 2, isotifs are shown for the branched chain four-center model (III) comprising the heavy atom skeleton of the urea molecule, carbon central. For Fig. 1, the calculations are based on the normal urea bond angles; for Fig. 2, angle OCN is increased to 150° to test the effect of anticipating the cyanic acid structure. In both cases, $\alpha$ should be quite small with respect to $\beta$ because the relative change in the carbonyl bonding is small in the reaction; similarly, $\gamma$ should be somewhat smaller than $\beta$ but of the same magnitude.[12] Chemical inference, then, suggests that acceptable values of

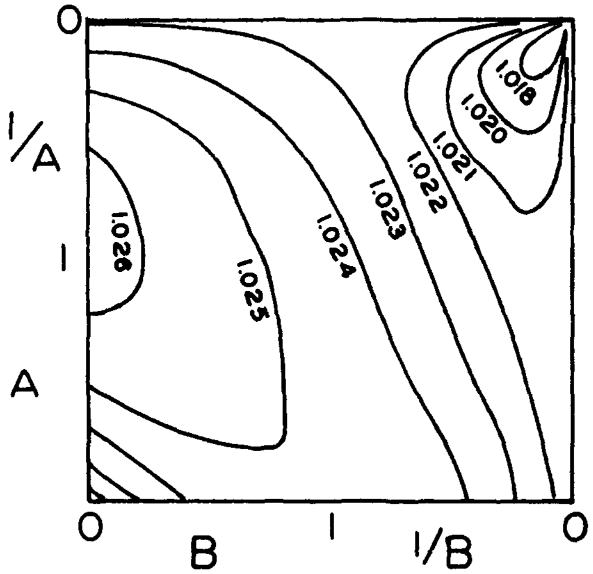


Fig. 1.—Isotifs, model III: $m_1 = 16$, $m_3 = 14$, $m_4 = 14$, $m_2 = 12$, $m_2' = 13$; $\phi_1 = 122.5°$, $\phi_3 = 122.5°$, $\phi_4 = 115°$.

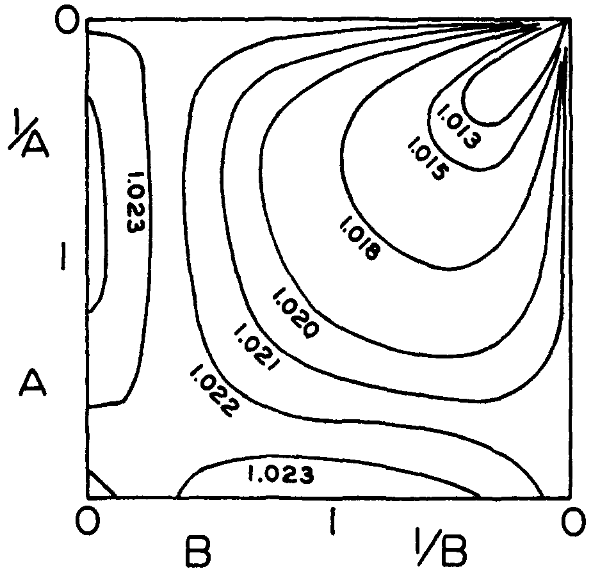


Fig. 2.—Isotifs, model III: $m_1 = 16$, $m_3 = 14$, $m_4 = 14$, $m_2 = 12$, $m_2' = 13$; $\phi_1 = 150°$, $\phi_3 = 105°$, $\phi_4 = 105°$.

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(12) For the case of Fig. 2, $\gamma$ should be more nearly equal to $\beta$ than for Fig. 1 because of the increase in angle OCN.

*A* lie near zero, while those expected for *B* lie near 1. The values of TIF in the regions so described are in the neighborhood of 1.023–1.025; the experimental value of 1.016 requires that *A* and *B* both be large, 1.5–10. Parameter values this large correspond, in the carbon central model, to greater C–O and C–N bond formation, respectively, than C–N bond rupture—as if upon activation the molecule became very compact before exploding into products; this is not an attractive picture of the hydrolysis.

Isotifs for two versions of the cyclic reaction coördinate similar to that suggested by Shaw and Bordeaux[13] are shown in Figs. 3 and 4. In the former, the bond angles are approximately those of the normal urea molecule, but the results depend but little upon the angle CNH; in the latter, it has been assumed that deformation accompanies activation, and all bond angles have been taken as 90°. In both cases, $\alpha$ should be somewhat smaller than $\delta$ but of the same magnitude; similarly, $\beta$ and $\delta$ should be approximately equal. Chemical inference, then, suggests that the acceptable values of *A* and *B* lie near 1 in an elliptical area near the center of each figure. Where the bond angles are normal, Fig. 3, the values of TIF in this region are 1.003–1.008; where deformation is assumed, Fig. 4, the TIF values lie in the range 1.007–1.016, and agreement with experiment is approached. Probably, it would not be difficult to achieve agreement in terms of this model between experimental and calculated temperature dependent factors in the isotopic rate constant ratio.

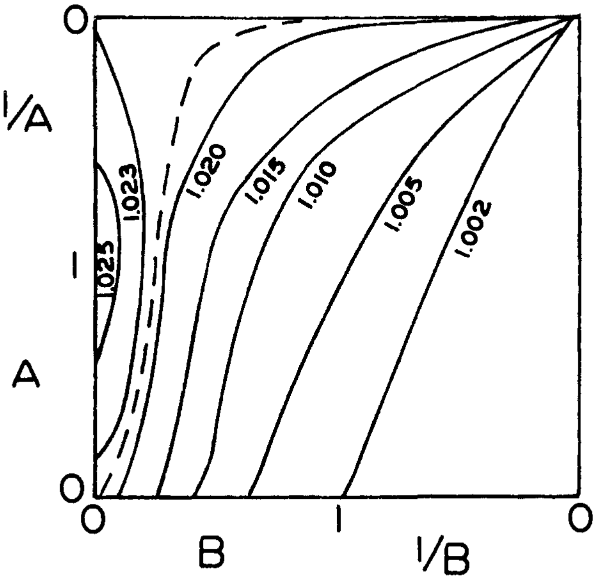

Fig. 3.—Isotifs, model II: $m_1 = 12$, $m_1' = 13$, $m_2 = 14$, $m_3 = 1$, $m_4 = 14$; $\phi_1 = 120°$, $\phi_2 = 110°$, $\phi_3 = 70°$, $\phi_4 = 60°$. The dashed line is the value (1.0214) expected for simple C–N bond rupture.

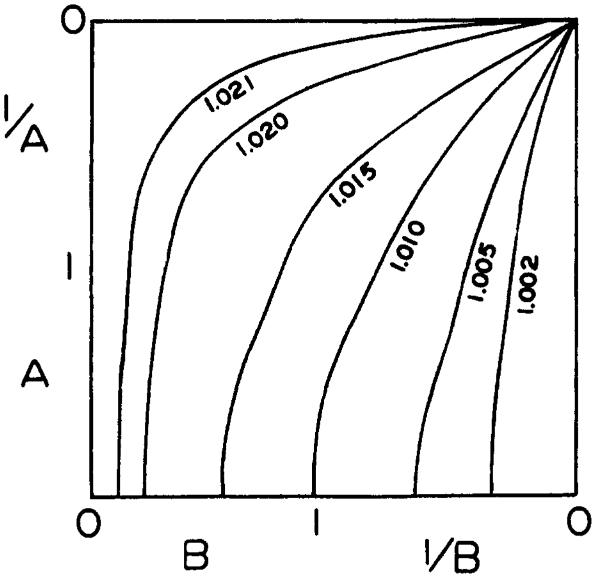

Fig. 4.—Isotifs, model II: $m_1 = 12$, $m_1' = 13$, $m_2 = 14$, $m_3 = 1$, $m_4 = 14$; $\phi_1 = \phi_2 = \phi_3 = \phi_4 = 90°$.

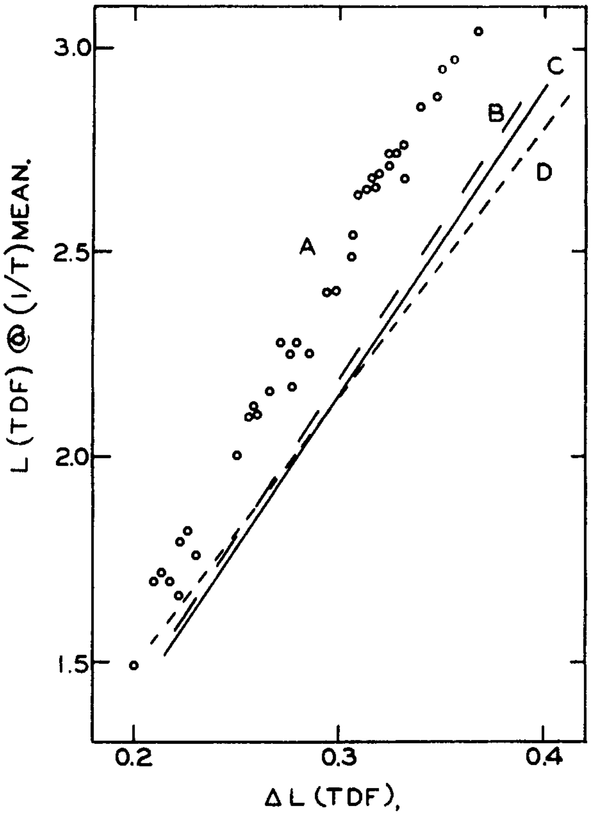

Fig. 5.—*L*(TDF) at mean (1/*T*) *versus* Δ*L*(TDF) for the temperature interval (1000/*T*) = 2.75–3.00, carbon 13 isotope effects: (A) 9-particle model for malonic acid and 8-particle model for mono-anion of malonic acid decarboxylation; all bond angles 120°; bond distances—Pauling's rule, force constants—Badger's rule; several different reaction coördinates assumed. (The circles represent the results of individual calculations; the scatter of the results is about average.) (B) – – – –, 3-particle and 4-particle models for urea hydrolysis; as in A, except that bond angles were variable and the reaction coördinate was closely simple bond rupture or an asymmetric stretching vibration. (C) ———, 3-particle model (carbon skeleton) for malonic acid decarboxylation, intramolecular isotope effect; parameter variation as in B. (D) ---------, similar to C, but for intermolecular isotope effect.

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[13] W. H. R. Shaw and J. J. Bordeaux, This Journal, **77**, 4729 (1955).

When the groupings O–C–N–H and N–C–N–H with normal bond angles are treated as in model I, the results are virtually identical with those shown in Fig. 3. For the N–C–N–H model, the predicted TIF, 1.022–1.025, is in the neighborhood of that for the C–N two-center model (1.0214) and high in comparison with experiment. For the O–C–N–H model, the predicted TIF is quite sensitive to the value assumed reasonable for $\gamma$. It seems likely that the change in the N–H bond upon activation is small compared with that in the C–N ($\beta$) bond which is being ruptured; however, the predicted TIF could correspond well with the experimental value if $B(=\gamma/\beta)$ were in the range 0.2–0.4.

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## Appendix

**"Experimental" Value of TIF.**[14]—The values of the temperature independent factor referred to above as "experimental" are obtained by the following semi-empirical method.

The system under study is described in terms of models for the normal and activated molecules. The various input parameters (particle masses, bond lengths, bond angles, force constants, label positions, nature of the reaction coördinate motion, etc.) are subject to systematic variation, each of many groupings of the variants leading finally to a calculation of TIF[15] and of TDF at two temperatures, well-separated, but within the range of the experiments. Values of $L(\text{TDF})$, $L = 100 \ln$, at the mean $(1/T)$ are plotted as ordinates *versus* the difference in $L(\text{TDF})$ between the two temperatures. The results of several such families of calculations are shown in Fig. 5. Use of these graphs depends upon the fact (eq. 1) that $L(k_1/k_2) = L(\text{TIF}) + L(\text{TDF})$. From the observed value of $\Delta L(\text{TDF})$ a figure for $L(\text{TDF})$ at the mean value of $(1/T)$ for the calculation interval is obtained; combination of this figure with $L(k_1/k_2)$ at that temperature yields an "experimental" value for $L(\text{TIF})$. Since TIF is a property of the reaction coördinate motion only, contributions of equilibria to TDF do not affect the applicability of the method to a large degree.

For all $u$ $(= hc\omega/kT) \geqslant 3$, there is but small error in the approximation $\sinh(u/2) = [\exp(u/2)]/2$. Using this approximation, it can be shown that at the temperature corresponding to the mean value of $(1/T)$ in the calculation interval $(T_1,T_2)$: $L(\text{TDF}) = c_1\Delta L(\text{TDF}) + c_2$; $c_1$ is a function of $T_1$ and $T_2$ alone, while $c_2$ is a relatively insensitive function of the models assumed for the normal and activated molecules. For several models to yield similar graphs as in Fig. 5, it is necessary that they have similar complexity, similar partial compensation for the effects of low frequencies and similar distributions of high and low frequencies. These are stringent criteria, and it is remarkable that the various calculations described in the caption to Fig. 5 yield plots no more divergent.

(14) It is important to note that TIF is *not* the ratio $A_1/A_2$ of isotopic Arrhenius *A*-factors.

(15) In general, these TIF values are abandoned for the present purpose. Of course, if a particular calculation based on a reasonable set of input parameters happened to yield good correspondence with the results of the experiments, the problem at hand would be solved. This is not often the case, and, since the temperature dependence and magnitude of the isotopic rate constant ratio are the quantities derived from experiment, our concentration on TDF is required.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

# Infrared Anisotropy and Structure of Crystalline Form C Stearic Acid and Vaccenic Acid[2]

BY H. SUSI

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The infrared spectra of highly oriented crystalline films of form C stearic acid and of vaccenic acid have been obtained using polarized radiation with the plane of polarization perpendicular and at 45° angles to the principal crystal planes. The anisotropy of stearic acid is discussed in relation to its known structure. The data obtained on vaccenic acid indicate that the substance crystallizes in the orthorhombic system. The factor group of the space group is probably isomorphous with $D_{2h}$. The main portions of the hydrocarbon chains are packed into an orthorhombic substructure similar to polyethylene and form C saturated acids, but the chains seem twisted near the double bonds, which appear to be nearly parallel in the projection along the *C*-axis.

## Introduction

The structure of saturated long chain monocarboxylic acids in their various crystallographic forms is known from single crystal X-ray measurements.[3] Very few data are available on the structure of the corresponding mono- and polyunsaturated compounds. Lutton and Kolp[4] have concluded from long spacing measurements obtained from powder diffraction data that in the *trans*-6- through *trans*-12-octadecenoic acids the hydrocarbon chains of the odd compounds are roughly perpendicular to the planes containing the carboxyl groups, whereas the chains of the even compounds are tilted. Odd and even refer to the number of carbons from the carboxyl group to the double bond.

(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented in part at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1958.

(3) E. v. Sydow, *Arkiv. Kemi*, **9**, 231 (1956).

(4) E. S. Lutton and D. G. Kolp, THIS JOURNAL, **73**, 2733 (1951).