TABLE I

ULTRAVIOLET SPECTRA IN AQUEOUS SOLUTION

Nickel Compounds			Copper Compounds		
	$\lambda_{max.}$ (mμ)	ϵ		$\lambda_{max.}$ (mμ)	ϵ
(I)[1]	436	104	(I)[3]	505	126
	282	5,400		260	6400
	213	17,300			
(II)[1]	436	70	(II)[3]	525	88
	268	2,100		244	5200
	205	15,000			
(III)	420	110	(III)	547	200
	265	2,260		263	5200
	218	14,000			

pared by the method of Jonassen and Douglas.[7] This material (3 g.), anhydrous acetone (100 ml.) and anhydrous zinc chloride (5 g.) were heated in a sealed tube at 110° for four days. On mixing the reactants the pink-violet crystals partially dissolved and the acetone solution became yellow. During the heating period yellow crystals of the cyclic tetrachlorozincate(II) complex formed on the walls of the tube. These yellow crystals were dissolved in a small amount of water, boiled with absorbing charcoal to remove any acetone polymers and, after filtration and evaporation to a small volume, poured into excess acetone. The precipitated bright yellow crystals were recrystallized from water–acetone solution; yield 30%.

Anal. Calcd. for $C_{12}H_{26}N_4NiZnCl_4$; Ni, 11.9; C, 29.3; H, 5.32; N, 11.4; Cl, 28.8. Found: Ni, 11.9; C, 29.0; H, 5.22; N, 11.3; Cl, 28.5.

1,5,8,11-Tetrazo-2,4,4'-trimethylcyclotrideca-1-ene Copper (II) tetrachlorozincate(II).—Equimolar amounts of copper-(II) chloride dihydrate and triethylenetetramine were mixed in a 50-50 ethanol–water solution. A bright blue solution resulted, and much heat was evolved, but on cooling and evaporation only a blue gum could be isolated. About 5 g. of this gum was stirred with anhydrous calcium sulfate until a thick paste was formed and as much water as possible was removed by storing this over concentrated sulfuric acid. The dry paste was heated with a further amount of anhydrous calcium sulfate and 100 ml. of anhydrous acetone in a sealed tube at 100° for 40 hr. (Heating at higher temperatures caused decomposition to copper metal.) At the end of the heating period the tube was cooled rapidly and the acetone poured from the solid gum. The acetone solution was evaporated and the residue boiled with water. After four treatments with decolorizing charcoal, a violet solution was obtained. On slow evaporation in the presence of excess zinc chloride solution, violet-black crystals of the tetrachlorozincate(II) salt were isolated. The gum remaining in the tube also contained some of the required product but was difficult to isolate from the starting material. The gum was dissolved in water, boiled with decolorizing charcoal and zinc chloride added to the resulting blue-violet solution. Dilute hydrochloric acid was added until the solution was just acid and on slow evaporation a further quantity of the final product was isolated. The combined products were dissolved in a little hot water and poured into a large excess of acetone. A fine violet powder was immediately precipitated; yield 40%.

Anal. Calcd. for $C_{12}H_{26}N_4CuZnCl$: Cu, 12.9; C, 29.0; H, 5.27; N, 11.2; Cl, 28.45. Found: Cu, 13.0; C, 28.9; H, 5.19; N, 11.0; Cl, 28.4.

Analysis.—Nickel was determined as its dimethylglyoxime derivative and copper as the salicylaldoxime complex, the complex cations (III) being decomposed by boiling peroxydisulfate solution. The Dumas method gave rather unsatisfactory nitrogen analyses and better results were obtained using the Kjeldahl method.

Spectra.—The visible and ultraviolet spectra were determined in aqueous solution using a Unicam model S.P. 500 spectrophotometer. The infrared spectra were determined in mulls, a Perkin–Elmer model 21 infrared spectrophotometer being used.

X-Ray Powder Diffraction Patterns.—These were obtained from a Phillips X-ray spectrograph coupled to a Brown recording potentiometer.

Acknowledgments.—The authors thank Dr. B. Cleverly of the Dominion Laboratory, Wellington, and the Chemistry Department, Canterbury University, Christchurch, for the infrared spectra determinations.

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[7] H. B. Jonassen and B. E. Douglas, *J. Am. Chem. Soc.*, **71**, 4094 (1949).

[CONTRIBUTION 1688 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

The Kinetics of the Thermal *cis-trans* Isomerization of 2-Methyl[2.1.0] bicyclopentane

BY JOHN P. CHESICK

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The kinetics of the reversible *cis–trans* isomerization reaction of 2-methyl[2.1.0]bicyclopentane have been studied between 203.3 and 231.7° and at reactant pressures between 0.08 and 1.7 mm. If the lower boiling isomer is tentatively identified as *trans*, then $K = k_{trans}/k_{cis} = 0.58$ at 220° for the *trans* → *cis* reaction. $/\Delta H/ \leq 0.5$ kcal./mole. $(k_{trans} + k_{cis}) = 10.^{14.45} \exp((-38.9 \pm 0.8 \text{ kcal.})/RT)\text{sec.}^{-1}$. The transition state is concluded to be one of incomplete rupture of the bridgehead–bridgehead bond corresponding to considerable residual bicyclic strain energy. The first order rate constants have decreased less than 10% on lowering the reactant pressure to 0.1 mm.

Introduction

As a consequence of a study of the kinetics of thermal isomerization of [2.1.0]bicyclopentane to cyclopentene,[1] it was observed that the activation energy was 46.6 kcal./mole, a number considerably larger than the value of 19 ± 4 kcal. calculated for the strength of the bridgehead–bridgehead bond assuming the extra bicyclic strain energy to be released in the transition state. A substituted bicyclo compound, such as the hitherto unreported 2-methyl[2.1.0]bicyclopentane (sometimes referred to as floor-methylhousane) would permit the observation of a probable *cis–trans* reaction which must require at least some loosening of the central bond. Since some low pressure drop-off of the first order rate constant was observed for the unimolecular reaction of the unsubstituted compound,[1] it was also of interest to study any *cis–trans* reaction at the lowest possible pressures to see whether methyl substitution had the expected effect

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[1] M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, to be published.

of increasing the number of oscillators or vibrational modes contributing as sources and sinks of energy in the reaction.

Experimental

The preparation of *cis* and *trans* 2-methyl[2.1.0]bicyclopentane was carried out by catalytic addition of methylene to 3-methylcyclobutene, a hitherto unreported compound.

Preparation of 3-Methylcyclobutene.—A 25 g. sample of 3-exomethylenecyclobutanecarboxylic acid[2] was hydrogenated in 250 ml. of ethyl acetate with 5 g. of 5% Pd on charcoal catalyst at room temperature and 50 lb. hydrogen pressure with the theoretical uptake of hydrogen to make 3-methylcyclobutanecarboxylic acid. After filtration, about three fourths of the solvent was removed under vacuum, and the procedure of Beard and Burger[3] was followed to make the 3-methylcyclobutane isocyanate by treatment of the acid with ethyl chloroformate, sodium azide and the thermal decomposition of the acid azide. The bulk of the toluene used as a solvent in the last step was removed under vacuum, and the concentrated toluene–isocyanate solution was heated under reflux with 240 ml. of 18% HCl for 12 hr. to produce the amine hydrochloride. The residual toluene was removed *in vacuo* and the aqueous phase was made basic with NaOH and extracted with five portions of hexane, totaling 300 ml. This amine solution was dried over Na_2SO_4, and the amine hydrochloride was precipitated with anhydrous HCl yielding 7.5 g. of precipitate. This precipitate was dissolved in water, made basic and exhaustively methylated following the procedure used by Applequist and Roberts[4] in preparing the exomethylene analog. The residue after evaporation of the solvents from the methylation was extracted with six portions of chloroform. Six g. of solids was left on removal of the chloroform. A sample of this was recrystallized from propanol and 2-butanol; m.p. 214.3–214.8° (dec).

Anal. Calcd. for $C_8H_{18}NI$: C, 37.66; H, 7.11; N, 5.49. Found: C, 37.67; H, 7.35; N, 5.50.

The bulk of the crude quaternary ammonium iodide was dissolved in a minimal amount of water and was shaken with moist silver oxide. After filtration of the solution under nitrogen, the quaternary hydroxide solution was concentrated *in vacuo*. This concentrated solution was added dropwise to a flask evacuated to 1 cm. at 160–170°, and the products of the Hofmann elimination were collected in a Dry Ice cooled trap. The pressure in the system was never allowed to rise above 2.5 cm. The small organic phase in the receiver readily distilled into a liquid nitrogen trap while the primary trap was held near Dry Ice temperature; this organic material was clear and low melting. Samples of the volatile material were subjected to g.l.p.c. analyses using a 6 m. dimethylformamide column and a silicone oil–silver nitrate combination column.[1] The sample eluted after acetylene on the first column and had a retention time on the second column which was reasonable for a C_5 mono-olefin. The hydrocarbon product was of better than 90% purity. All 60 Mc. n.m.r. spectra reported here were taken as less than 10% solutions in carbon tetrachloride, with tetramethyl silane as an internal standard, and chemical shifts are reported as τ values.[5] The principal g.l.p.c. peak, the supposed 3-methylcyclobutene, showed a sharp proton resonance at $\tau = 4.2$, corresponding to the vinyl protons. Principal peaks of a multiplet structure, attributed to three nonvinyl cyclobutane hydrogens, were found at 7.27, 7.48, 7.56, 8.0 and 8.2. A sharp doublet methyl resonance at 8.91 proved that the compound was the 3-methyl and not the 1-methyl isomer. The area ratios of the three groups of peaks were close to the expected 2:3:3 proportions. Wiberg and Nist[6] report 4.03 and 7.46 as the positions for vinyl and methylene proton resonances in cyclobutene, corroborating the above assignments. Gas phase infrared spectra taken with a Perkin Elmer Model 221 showed bands at 3130, 3060 and 1570 cm.$^{-1}$, in addition to other bands. This agrees with Lord and Rea's[7] report of 3126, 3048 and 1566 cm.$^{-1}$ for modes corresponding to symmetric and antisymmetric vinyl hydrogen stretch and vinyl carbon-carbon stretch in cyclobutene.

Preparation of 2-Methyl[2.1.0]bicyclopentane.—The catalytic action of metals in reactions of diazo compounds has been known for some time. The use of cuprous chloride to catalyze the reaction of diazomethane with olefins to give cyclopropanes has been reported.[8] Much recent work in this Laboratory[9] has shown that only the expected products of methylene addition to the double bond occur when diazomethane is passed through a solution of an olefin in the presence of cuprous chloride. No insertion products, such as one obtains from reactions of photochemically produced methylene with hydrocarbons, are found. Hence the established procedure for catalytic methylene addition was followed in the reaction starting with 3-methylcyclobutene. One g. of 3-methylcyclobutene was dissolved in 10 ml. of pentane in a small volume reaction vessel fitted with Dry Ice condensers, magnetic stirrer and gas inlet tube which reached near the bottom of the vessel. A nitrogen gas stream carried the diazomethane, generated from N-nitroso-N-methylurea and aqueous KOH and dissolved in a decalin layer, into the olefin solution which was cooled by an ice bath. About 0.2 g. of anhydrous cuprous chloride was added to the olefin solution before starting the reaction. Thirty five g. of urea was added to the generator in one gram lots. Analysis of the product mixture using silicone oil and carbowax g.l.p.c. columns showed two products in the C_6 region, differing sufficiently in boiling point to permit peak resolution. The ratio of low boiling to high boiling products was 2.0/1. The materials in each of the two peaks had very similar gas phase infrared spectra, which were also similar in many features to the spectrum of authentic [2.1.0]bicyclopentane[1]; the behavior in the g.l.p.c analyses of either peak on use of varying lengths of silver nitrate column, and the absence of vinyl protons in the n.m.r. spectra attest to the absence of double bonds. The n.m.r. spectrum of the early eluting peak, or the lower boiling product, showed a moderately sharp peak at $\tau = 7.9$, a broad multiplet centered at 8.5, a sharp doublet centered at 8.8 and another peak at 9.45. This may be compared with the n.m.r. spectrum of [2.1.0]bicyclopentane which has three groupings of resonances centered at $\tau = 7.9$, 8.6 and 9.5, corresponding to bridgehead, cyclobutyl and cyclopropyl hydrogens, respectively. The late eluting, higher boiling, product had an n.m.r. spectrum in which the sharp doublet due to methyl protons was shifted upfield to 9.2, and the resonance at 7.9 found in the spectrum of the lower boiling isomer was broadened or replaced by multiplets at 6.2 and 7.6. The doublet nature of the methyl peak precludes a bridgehead location. The method of synthesis would seem to eliminate the remaining cyclopropane carbon as a position for the methyl group. Infrared spectra were also consistent with a cyclopropyl CH_2 group. Hence it is concluded that the two products from the diazomethane synthesis comprise the *cis* and *trans* isomers of 2-methyl[2.1.0]bicyclopentane. Since the specific assignment of *cis* or *trans* structure to a particular isomer is quite uncertain and is not vital to the purposes of this work, all further discussion of the two isomers will refer to them using the experimental designations of E, for the Early eluting, lower boiling form, and L for the Later eluting, or higher boiling form. Some consideration will be given later to the problem of structure assignments.

A 1.3-cm. o.d., 2-m. silicone oil on firebrick preparative g.l.p.c. column was used in preliminary separations of E and L from the pentane solvent, and final separations and purifications were made using an 8-mm. o.d. silicone oil–silver nitrate combination column. It was found necessary to operate the preparative column at temperatures below about 50° to avoid isomerization of E and L on the column to appreciable amounts of three substances which were mono-olefinic and which probably were the three isomeric methyl cyclopentenes. No problems of this nature were observed in the separations or kinetic run analyses using the combination column at room temperature.

Kinetic Measurements.—The vacuum system and 500 ml. thermostated reaction vessel and general procedures were the

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[2] Supplied through the courtesy of Dr. H. E. Simmons, E. I. du Pont, Inc. Material for the final kinetic runs was prepared by a repetition of this procedure using 3-methylcyclobutanecarboxylic acid prepared by Mr. Moser, Department of Chemistry, Yale University.

[3] C. Beard and A. Burger, *J. Org. Chem.*, **26**, 2335 (1961).

[4] D. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4012 (1956).

[5] G. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[6] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

[7] R. C. Lord and D. G. Rea, *ibid.*, **79**, 2401 (1957).

[8] P. Gaspar, Ph.D. thesis, Yale University, 1961.

[9] Wm. von E. Doering and W. Roth, private communication.

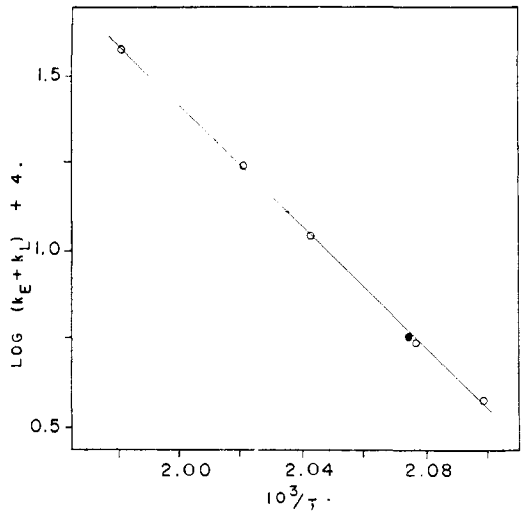

Fig. 1.—An Arrhenius plot of $(k_E + k_L)$: ○, unpacked vessel; ●, packed vessel.

same as previously described,[10] with the exception that a 3-m. Dow Corning 710 silicone oil on Celite column was used in series with 0.9-m. of silver nitrate in ethylene glycol on firebrick at room temperature for the g.l.p.c. analyses. The E material used was of greater than 99.8% purity, and the L material usually had about 2% of E as an impurity because of some tailing of the E peak when larger quantities of material were passed through the column. The E and L fractions were trapped in the course of run analysis, and they were reused to conserve the starting material after repassage of the collected materials through the column. No buildup of minor products occurred in this procedure since both E and L fractions gave essentially the same equilibrium mixture at high temperatures, and the second batch of E and L synthesized gave the same kinetic results as the first quantity of material which had been reused many times.

Results

The residual pressure in the vacuum manifold and reaction vessel after trapping the reaction products was always less than 0.1 micron, hence there was no observable noncondensable gas, *i.e.*, hydrogen or methane, formed in the reaction. The pressure of the products in the vacuum system was measured after run completion, and the ratio of product to reactant pressure was independent of degree of reaction to within the precision of the pressure measurement, about 5%, indicating the absence of significant polymerization reactions. Three runs in which the surface to volume ratio was increased by a factor of 55 by packing the reaction vessel with 4 mm. dia. glass beads gave a mean rate constant within 3% of the rate constant obtained from the Arrhenius plot for runs with the unpacked vessel. It is therefore concluded that the rate constants calculated in this work are for the homogeneous reaction.

Further evidence that E and L form a pair of isomers undergoing a reversible interconversion is the identity of the Product L′ produced by the thermal reaction of E with the L produced in the synthesis, and likewise for the E′ produced from L decomposition. G.l.p.c. retention times and infrared spectra were in perfect agreement for E′ and E and for L′ and L. The attainment of the same equilibrium mixture in a series of seven runs at 242.8° using both starting materials, previously cited in another context, also demonstrates the isomeric structures and readily interconvertible nature of E and L at elevated temperatures. At the lower end of the reaction temperature scale it was not practical to wait for attainment of equilibrium, and one must here rely on the ability to fit the data for either starting material and various degrees of conversion using only the two first order rate constants for the forward and reverse reactions. The ratio of these rate constants is the equilibrium constant in such a reaction scheme. Using the average $K = 0.57$ from the ratio L/E at equilibrium at 242.8°, and the value $K = 0.60$ used to fit the kinetic data at 203.3°K., one obtains $\Delta H = -0.5$ kcal./mole and $\Delta S = -2.1$ e.u. for the E to L reaction. The K values used to fit rate data at intermediate temperatures lie between these values of 0.60 and 0.57. The error in ΔH. and hence in ΔS, calculated from this procedure is probably 50 to 100%. The difference in energy between the two isomers is too small to be significant in the Arrhenius plot of the rate constants, and hence such a plot could be made for the sum of the first order rate constants $(k_E + k_L)$; the label designates the reactant species. Figure 1 is an Arrhenius plot of $(k_E + k_L)$; this sum is computed from the integrated rate equation for a reversible first order reaction. Values for $K = k_E/k_L$ are selected to give the best fit for data from both E and L runs. Only at high conversion is $(k_E + k_L)$ highly sensitive to both the value of K and to the uncertainty in the product analyses. Each point on the plot represents an average of four to ten runs at varying degrees of reaction with a mean number of seven runs per temperature and using both E and L as starting materials. A mean activation energy of 38.9 kcal./mole is obtained for $(k_E + k_L)$. Using $\Delta H = -0.5$ kcal./mole for the E → L reaction

$$k_E = 0.80 \times 10^{14} \exp(-38.65 \pm 0.8 \text{ kcal.}/RT) \text{ sec.}^{-1}$$
$$k_L = 2.31 \times 10^{14} \exp(-39.15 \pm 0.8 \text{ kcal.}/RT) \text{ sec.}^{-1}$$

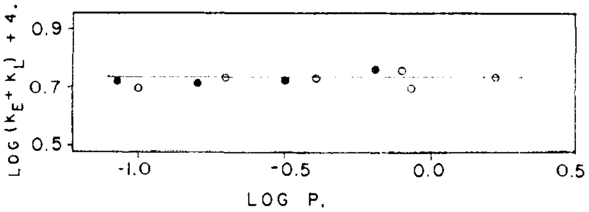

Fig. 2.—Pressure dependence of $(k_E + k_L)$: ○, E as starting material; ●, L as starting material; T, 208°.

A plot of log $(k_E + k_L)$ *vs.* log P for the series of runs covering the greatest pressure range, the runs at 208.3°, is shown in Fig. 2.

There is little if any significant fall in $(k_E + k_L)$ down to 0.1 mm., and it is concluded that the reaction has been studied in the high pressure region.

Discussion

The primary purposes of the work, determination of the energy barrier and low pressure behavior, do not demand assignment of the *cis* form to E or L. The E form is slightly higher in both energy and entropy than L and is the lower boiling isomer. Rather crude models indicate that there is not a clear distinction between *cis* and *trans* forms with

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[10] J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, to be published.

respect to steric hindrance of the methyl group. Therefore the small observed ΔH does not materially aid the structure assignment. Using very simple models, the *cis* form seems to have more carbon–hydrogen bonds oriented toward one side of the four membered ring than does the *trans* form. If the source of the total dipole moment is considered to be the vector addition of CH bond moments of about 0.3D. each,[11] then the *cis* form may be thought to have a slightly higher dipole moment and therefore a higher boiling point than the *trans* form. This argument would then suggest that the L isomer has the *cis* structure. The clearest difference in the n.m.r. spectra is the upfield shift, $\Delta\tau = 0.4$, in the methyl proton doublet in going from the E to the L form. In the *cis* form the methyl is over the plane of the cyclopropane ring, whereas in the *trans* form the methyl group is more nearly coplanar with the cyclopropane ring. The magnetic anisotropy of benzene is such that protons above the plane of the aromatic ring experience stronger shielding than protons in the plane,[12] and resonance occurs at higher fields. The cyclopropane ring is somewhat analogous in allowing a similar anisotropy through ring currents. This argument would therefore also suggest that L is the *cis* form.

Previous thermochemical calculations[1] have indicated that $\Delta H = 19 \pm 4$ kcal. for the formation of a cyclic diradical with relief of the bicyclic strain and without bonding across the former bridgehead carbon atoms, starting from the bicyclopentane ring system. The 38.9 kcal. found for the barrier to isomer interconversion then indicates an appreciable amount of cross ring bonding in the transition state so that the strain is far from completely relieved.

The analogy between this reaction and the geometric isomerization of cyclopropane-d_2 studied by Schlag and Rabinovitch[13] may be noted. The transition state required by the energetics of this *cis–trans* reaction suggests that the trimethylene biradical mechanism A. discussed in connection with the cyclopropane-d_2 *cis–trans* reaction,[13] is an extreme viewpoint, and the fruitful picture is one in which fairly strong interactions between the ends of the "trimethylene" are considered, *i.e.*, the compromise between mechanism A and the mechanism B involving a co-planar CH_2 and ring, as discussed in refs. 8 and 10 of Schlag and Rabinovitch.

This isomerization reaction and the structural isomerization of [2.1.0]bicyclopentane to cyclopentene were both studied under conditions giving comparable values of the parameter $b = E/RT$. Both reactions have similar A factors; therefore, the pressure dependencies may be compared directly. The observation of less than 10% decrease in rate constant on reduction of pressure to less than 0.1 mm. corresponds to an increase in the Kassel or Slater S parameters of at least six relative to bicyclopentane. An increase in the lifetime of an activated species before reaction of at least thirty is then deduced. These comparisons assume similar pressure behavior for the *cis–trans* reaction and the structural isomerization of methylbicyclopentane to the methylcyclopentenes. This assumption seems reasonable since the geometrical and structural isomerization reactions of cyclopropane have been demonstrated to have similar pressure dependencies.[13] The effect of methyl substitution on the lifetime of the activated bicyclopentane molecule and hence on the rate pressure dependence is of the same magnitude as the effects of methyl substitution on the pressure dependencies of the cyclopropane[14] and cyclobutane[15] reactions. Thus more evidence has been obtained which seems to indicate that after taking into account variations in the A and E factors, the total number of atoms in the molecule is the chief factor determining the initial (observable) part of the low pressure dropoff of rate constants in thermal unimolecular reactions of small hydrocarbon molecules.

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(12) J. Pople, W. Schneider and H. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 180-183.

(13) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).

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(15) M. N. Das and W. D. Walters, *Z. Physik. Chem.* (*Frankfurt*), **15**, 22 (1958).