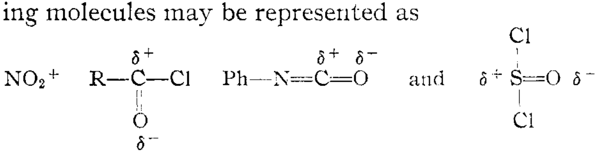
cedure after $[Co(en)_3]Cl_3$ had been removed by dilution with ethanol.

It is also interesting that all compounds reported here have a distinct red color. It is generally found that the coördination of six nitrogens about a cobalt(III) ion results in a yellow compound. The unusual shift to red would indicate an extensive effect of the OH group on the metal ion. This interaction is also supported by the very large change in reactivity of the hydroxy group toward organic reagents. None of the reagents tested were found to attack the hydroxy group.

It seems unlikely that direct coördination of the OH to cobalt has occurred. This would imply that cobalt may assume a coördination number of nine in $[Co(etolen)_3]^{+3}$ and eight in $[Co(etoldien)_2]^{+3}$. Complexes showing various, large coördination numbers would not be expected to have stabilities comparable to that of $[Co(en)_3]Cl_3$, as is observed here. It is equally as unlikely that cobalt(III) retains its coördination number of six by coördination of OH leaving a free amine group. Such a free amine would be as reactive as a free hydroxy group.

Inspection of molecular models suggests that if the two nitrogens of each of the three N-hydroxyethylethylenediamines are coördinated to the metal, the three free hydroxy groups will be in a very favorable position for hydrogen bond formation with the hydrogen of the coördinated nitrogen atom. The strong inductive effects resulting from the hydrogen bond may distort the field of the nitrogen with a resulting shift in spectrum.

The lack of chemical reactivity of the hydroxy group is not surprising in view of the mechanism generally accepted for attack by the reagents investigated. The functional groups of the attacking molecules may be represented as



$$NO_2^+ \qquad R-\underset{\underset{\delta^-}{\overset{\|}{O}}}{\overset{\delta^+}{C}}-Cl \qquad Ph-N=\overset{\delta^+}{C}=\overset{\delta^-}{O} \qquad \text{and} \qquad \delta^+\,\overset{Cl}{\underset{Cl}{S}}=O\ \delta^-$$

The reaction is initiated by the attack of the positive center of the reagent on an electron pair of the hydroxy oxygen. Models show the oxygen of the OH lies close to the cobalt(III) ion. Such a position places it in the large positive field of the cobalt. The activation energy necessary for the approach of a positive center into the positive field of the ion would be large and attack would be greatly hindered or prevented.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Metal Binding of the Benzimidazoles[1]

BY THOMAS J. LANE, C.S.C., AND KENNETH P. QUINLAN[2]

RECEIVED JUNE 8, 1959

The acid dissociation constants have been determined potentiometrically for benzimidazole, 2-methylbenzimidazole and 2-ethylbenzimidazole in solutions of ionic strength 0.16 *M* ($NaNO_3$) at 4 ± 1, 25 ± 0.1 and 35 ± 0.1°. The changes in enthalpy, ΔH^0, were found to be 8.7, 9.8 and 9.3 kcal./mole, respectively. Formation constants have been determined for copper(II) with benzimidazole by the Bjerrum potentiometric method in solutions of the same ionic strength at the three above temperatures. An upper limit of the value of the formation constant for copper(II) and 2-methylbenzimidazole at 4° is reported. The formation constants for cadmium with benzimidazole and 2-methylbenzimidazole have been determined by the polarographic method in 50% aqueous ethanol at 25 ± 0.1°. Results indicate that the benzene portion of the benzimidazole hinders coördination with copper(II). Formation constants of copper(II) with 2-hydroxymethylbenzimidazole and 1-methyl-2-hydroxymethylbenzimidazole show that the unsaturated nitrogen is the active site in the substituted benzimidazoles.

Introduction

No formation constants have been reported for metal complexes of benzimidazole and its alkylated derivatives although the substituted benzimidazoles have been thoroughly studied as analytical reagents[3-5] and as part of the Vitamin B_{12}[6] molecule.

Freiser[4] has postulated that the benzene part of the substituted benzimidazoles exhibits steric effects in the chelation of metallic ions. A comparison of the difference in the stability constants of the imidazoles[7] with those of the benzimidazoles may give conclusive evidence that the benzene portion of the molecule is sterically hindering the coördination.

It has been assumed that coördination with the substituted benzimidazoles takes place through the unsaturated nitrogen. Freiser's[8] infrared study on the chelates of the derivatives of benzimidazole seems to substantiate this assumption. A study of the steric effect of the methyl group on the stability constants of 2-hydroxymethylbenzimidazole and 1-methyl-2-hydroxymethylbenzimidazole was undertaken to show which of the two nitrogen atoms in the benzimidazole is coördinating.

Experimental

Materials, Apparatus and Solutions.—Benzimidazole, 2-methylbenzimidazole and 2-ethylbenzimidazole were obtained from the Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. The compounds were recrystallized at least three times before use and then purity was established by analysis and melting points.

---

[1] Presented at the 135th meeting of the American Chemical Society, Boston, Mass., 1959.

[2] The paper was abstracted from the Ph.D. thesis of Kenneth P. Quinlan, Notre Dame University, 1959.

[3] R. G. Charles and H. Freiser, *Anal. Chim. Acta*, **11**, 1 (1954).

[4] W. D. Johnston and H. Freiser, *ibid.*, **11**, 301 (1954).

[5] J. L. Walter and H. Freiser, *Anal. Chem.*, **25**, 127 (1953).

[6] M. T. Davies, P. Mamalis, V. Petrow, B. Sturgeon, G. H. Beaven, E. R. Holiday and E. A. Johnson, *J. Pharm. Pharmacol.*, **4**, 448 (1952).

[7] Y. Nozaki, F. R. N. Gurd, R. F. Chen and J. T. Edsall, THIS JOURNAL, **79**, 2123 (1957).

[8] T. R. Harkins, J. L. Walter, O. E. Harris and H. Freiser, *ibid.*, **78**, 260 (1956).

2-Hydroxymethylbenzimidazole was prepared by the Phillips method.[9] Equimolar amounts of *o*-phenylenediamine and glycolic acid were refluxed in 4 *N* HCl for 0.5 hr. The purity was determined by analysis and melting point.

1-Methyl-2-hydroxymethylbenzimidazole was prepared by the method of Hughes and Lions.[10] 2-Hydroxymethylbenzimidazole was treated with dimethyl sulfate, with the subsequent addition of sodium hydroxide. The anhydrous compound melted at 145.5–146.5 (lit. 143–144°).

Anal. Calcd. for $C_9H_{10}N_2O$: C, 66.72; H, 6.19. Found: C, 66.5; H, 6.4.

Sodium, potassium and cadmium nitrates were "Baker Analyzed" reagents; Triton X-100, Rohm and Haas Company, Philadelphia, was used as maximum suppressor.

Stock solutions of metallic ions were prepared and titrations were carried out as described by Freiser, Charles and Johnston.[11]

Fifty-five ml. of 0.32 *M* $NaNO_3$ solution, 50 ml. of 0.01 *N* nitric acid and 5 ml. of 0.01 *M* metal solution were added to a weighed quantity of ligand under study. The ligand to metal ratio was 8:1. The total ligand concentration was approximately 5×10^{-3} *M*. Standardized sodium hydroxide (0.1 *N*) was added in small increments to the stirred solution. After each addition of base the *p*H of the solution was taken. Attainment of equilibrium was checked by successive *p*H determinations.

Polarographic Measurements.—Current–voltage measurements were made with a Sargent XXI Polarograph. The capillary (S-29419) had a value for $m^{2/3}t^{1/6}$ of 2.49 at a potential of 0.5 volt and mercury height of 58.4 cm. in a stock solution (described below) 0.1228 *M* in benzimidazole. An "H" cell was used with an agar plug 1 *M* with respect to potassium nitrate. The potentials were measured to the nearest millivolt with a Rubicon potentiometer. All measurements were made at 25 ± 0.1°.

A stock solution of 50% aqueous ethanol containing 1×10^{-3} *M* $Cd(NO_3)_2$, 0.16 *M* KNO_3 and 0.004% Triton X-100 was prepared. An amount of the benzimidazole under study was dissolved in an aliquot of this aqueous ethanolic solution to give a solution which was slightly less than saturated. The concentrations of the benzimidazole and 2-methylbenzimidazole were 0.40 and 0.37 *M*, respectively. Polarograms were obtained for solutions containing varying amounts of the benzimidazole by successive dilutions with the stock solution containing no benzimidazole.

Oxygen was removed from all the solutions by lamp nitrogen prior to polarographic measurement.

Copper Chelates of the 2-Hydroxymethylbenzimidazoles.—An aqueous solution of copper(II) nitrate (0.008 mole) was treated with an alcoholic solution of 2-hydroxymethylbenzimidazole (0.017 mole) or 1-methyl-2-hydroxymethylbenzimidazole (0.017 mole). The solutions were made basic by the dropwise addition of ammonium hydroxide. A bluish precipitate was obtained in the case of 2-hydroxymethylbenzimidazole. The copper chelate of 1-methyl-2-hydroxymethylbenzimidazole was precipitated on standing in the cold. The precipitates were filtered, washed with ethyl alcohol and dried for 3 hr. at 100°. The chelates were decomposed with perchloric and nitric acid mixture and the copper content was determined by electrodeposition.

The analysis of the copper(II) chelates of 2-hydroxymethylbenzimidazole and 1-methyl-2-hydroxymethylbenzimidazole indicated a ligand to metal ratio of 1:1 and 2:1, respectively.

Results

Dissociation Constants.—Table I shows the *pK′* values for the dissociation of the protonated benzimidazoles and the 2-hydroxymethylbenzimidazoles. The ionic strength was adjusted with sodium nitrate. The *p*H value at the stoichiometric midpoint of the titration of the protonated reagent was taken as being equal to the *pK* of the basic nitrogen. The *pK* values were converted to the apparent acid dissociation constants, *pK′*, for the particular ionic strength by means of the activity coefficient, 0.81, for the hydrogen ion.[12] In a similar manner the *p*H at the stoichiometric midpoint of the titration of the hydroxyl group was taken to be equal to the *pK* of the acid group, after corrections were applied to the hydrolysis of the reagent. In this range of *p*H values the sodium ion corrections were applied in all cases. Several solutions of the same ligand were run and these all agreed within ± 0.02 *pK* unit.

TABLE I

APPARENT DISSOCIATION CONSTANTS FOR THE LIGANDS AT IONIC STRENGTH OF 0.16 *M* ($NaNO_3$) AND AT VARIOUS TEMPERATURES

	pK'_{NH} 4 ± 1°	pK'_{NH} 25 ± 0.1°	pK'_{NH} 35 ± 0.1°	pK'_{OH} 25 ± 0.1°
Benzimidazole	6.00	5.58	5.36	...
2-Methylbenzimidazole	6.96	6.29	6.18	...
2-Ethylbenzimidazole	6.90	6.27	6.14	...
2-Hydroxymethylbenzimidazole	..	5.40	..	11.55
1-Methyl-2-hydroxymethylbenzimidazole	..	5.55	..	11.45

The *pK′* values obtained in the present investigation agree closely with those recorded in the literature. Davies[13] reported values of 5.48, 6.19 and 6.20 at 25° for benzimidazole, 2-methylbenzimidazole and 2-ethylbenzimidazole, respectively. These values are slightly lower than the ones recorded here since the present work was carried out at a higher ionic strength.

Values for ΔH^0 of 8.7, 9.8 and 9.3 kcal./mole were obtained for benzimidazole, 2-methylbenzimidazole and 2-ethylbenzimidazole, respectively. The maximum error in ΔH^0 is of the order of ± 1.0 kcal. The heats of dissociation for the benzimidazoles are greater than those of the imidazoles.[7] Therefore, the greater basicity of the imidazoles is an entropy effect. The difference between the standard free energy and the standard heat of dissociation for the benzimidazoles indicates a small positive entropy change for the ionization. The standard entropy change for the imidazoles was in all cases negative and of the order of -6 cal. deg.$^{-1}$ mole^{-1}.

The greater basicity of the 1-methyl-2-hydroxymethylbenzimidazole than that of 2-hydroxymethylbenzimidazole is probably the result of the inductive effect of the methyl group in the 1-position.

Association of Metals with Benzimidazole, 2-Methylbenzimidazole and 2-Ethylbenzimidazole.—The association of the metals Cu(II), Ni(II), Pb(II), Co(II), Zn(II) and La(III) with the benzimidazoles was studied by the Bjerrum[14] potentiometric technique. The only systems that exhibited coördination before metal hydrolysis were Cu(II) with benzimidazole and with 2-methylbenzimidazole. These were studied at different temperatures.

---

[9] M. A. Phillips, *J. Chem. Soc.*, 2820 (1929).

[10] G. K. Hughes and F. Lions, *J. Proc. Roy. Soc., N. S. Wales*, **71**, 209 (1938).

[11] H. Freiser, R. G. Charles and W. D. Johnston, THIS JOURNAL, **74**, 1383 (1952).

[12] J. Kielland, *ibid.*, **59**, 1675 (1937).

[13] M. T. Davies, P. Mamalis, V. Petrow and B. Sturgeon, *J. Pharm. Pharmacol.*, **3**, 420 (1951).

[14] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution " P. Haase and Son, Copenhagen, 1941.

Values of the average number of ligands bound per metallic ion, $\bar{n}$, were found from the relationship

$$\bar{n} = \frac{T_{\mathrm{Bz}} - \mathrm{BzH}^+ \dfrac{K + \mathrm{H}^+}{\mathrm{H}^+}}{T_{\mathrm{M}}}$$

where K is the acid dissociation constant of the protonated benzimidazole, T_{Bz} is the total initial concentration of the benzimidazole and T_{M} is the total concentration of the metal M. The concentrations of the protonated benzimidazole, BzH^+, were found from the expression

$$\mathrm{BzH}^+ = \mathrm{OH}^- + \mathrm{NO_3}^- - \mathrm{H}^+ - \mathrm{Na}^+$$

The negative log of the free ligand concentration pBz was found from the values of BzH^+ and the acid dissociation constant.

Log k values were calculated by the method of Scatchard[15] modified by Li, White and Doody.[16]

The coördination number, N, of copper with benzimidazole was taken as four. Plots of $\bar{n}$ *versus* pBz at 4 ± 1° gave a value of $\bar{n}$ close to three prior to the hydrolysis of the copper ion. The shape of the formation curves indicated that the coördination number of copper with benzimidazole was greater than three.

The log k_1, k_2, k_3 and k_4 values for copper(II) with benzimidazole at 4 ± 1° were 3.82, 3.35, 2.86, 2.4 and at 25 ± 0.1° were 3.43, 2.98, 2.51 and 2.0, respectively. At 35° the formation constants for this chelate were obtained by extrapolation and were lower than the values at 25° by approximately 0.3 log unit.

The standard enthalpy change for the first step for the reaction of copper and benzimidazole was calculated to be −9.0 ± 1.0 kcal./mole. This value is higher than −6.7 kcal./mole, found for the reaction of Cu(II) with 4-methylimidazole,[7] even though the log k_1 for the 4-methylimidazole is higher. The lower value of log k_1 for benzimidazole and copper(II) is the result of an unfavorable entropy term.

Chelation of Cu(II) with 2-Hydroxymethylbenzimidazoles.—The log k_1 values of the copper complexes of 2-hydroxymethylbenzimidazole and 1-methyl-2-hydroxymethylbenzimidazole in aqueous medium ($\mu = 0.16$) at 25 ± 0.1° were found to be 9.30 and 9.66, respectively. Formation curves for the two systems showed $\bar{n}$ approaching a limiting value of one, indicating the formation of a 1:1 complex. The value of $p\mathrm{R}^-$ at $\bar{n} = 0.5$ was taken to be equal to log k_1.

The solid chelate of 2-hydroxymethylbenzimidazole with copper(II) indicated a ligand to metal ratio of 1:1 whereas that of 1-methyl-2-hydroxymethylbenzimidazole showed a 2:1 ratio. This difference may be explained by the higher stability of the 1-methyl-2-hydroxymethylbenzimidazole chelate.

Polarographic Results.—The average values of the slopes of $\log(i_{\mathrm{d}} - i)/i$ *versus* $E_{\mathrm{d.e.}}$ for cadmium(II) complexes with the benzimidazoles in 50% aqueous alcohol solution was 0.03 (± 0.001), indicating reversible reactions for a 2 electron reduction. The half wave potential for the simple cadmium(II) ion (0.562 v.) shifted to more negative values on addition of varying amounts of ligand. A study of variation of i_{d} as a function of height of mercury gave an average value of 0.575 ± 0.003, indicating the current was diffusion controlled.

Plots of $E_{1/2}$ *versus* log C_{Bz} were used to calculate the number of groups, p, coördinated to the cadmium ion. Formation constants were calculated by

$$(E_{1/2})_{\mathrm{c}} - (E_{1/2})_{\mathrm{s}} = -\frac{RT}{nF} \ln k_{\mathrm{f}} - p\,\frac{RT}{nF} \ln C_{\mathrm{Bz}}$$

For cadmium(II) with benzimidazole these were: log k_1 = 2.00, log k_2 = 1.42 and log k_3 = 1.02; and for cadmium(II) with 2-methylbenzimidazole, log K_1 = 1.37.

The plots obtained for benzimidazole with Cd(II) consisted of three lines. The straight lines gave slopes whose values of p were 0.99, 1.90 and 2.88 corresponding to the species CdBz^{++}, $\mathrm{CdBz_2}^{++}$ and $\mathrm{CdBz_3}^{++}$, respectively. The $\mathrm{CdBz_3}^{++}$ species existed in the widest concentration range of 0.40 to 0.09 M. The di-coördinated species existed in the range of 0.09 to 0.04 M and CdBz^{++} below 0.04 M.

The cadmium 2-methylbenzimidazole data showed that only one complex existed in the range (0.37–0.00 M) studied. The value of p (1.08) corresponded to the species CdMeBz^{++}.

Discussion

The results of the present study show that benzimidazole and its alkylated derivatives form less stable coördination compounds than those of the imidazoles.[7] This is the result of two factors: (1) the pK's of the imidazoles are greater than those of the benzimidazoles; (2) the bulky benzene ring attached to the imidazole system in the benzimidazoles probably decreases their stabilities.

Freiser[4] has suggested that the benzene portion of the 2-substituted benzimidazoles interferes sterically with chelation. The present results compared to those for 4-methylimidazole[7] and 2,4-dimethylimidazole[7] indicate that the benzene portion offers some steric hindrance. In the association of metal ions with the 4-alkylated imidazoles, the methyl group is considered to be in the 4-position with the coördinating nitrogen in the 1-position as has been pointed out by Edsall.[7] The $\Delta pK'$ for 4-methylimidazole (7.54) and 2,4-dimethylimidazole (8.38) is 0.84 pK' unit. The difference in their log k_1 values for the copper complex is 0.3, the 4-methylimidazole having the greater affinity for copper. A maximum value of log k_1 (2.6) has been obtained for the copper(II) 2-methylbenzimidazole complex at 4° which when extrapolated to 25° would be about 2.2. The $\Delta pK'$ for benzimidazole and 2-methylbenzimidazole (Table I) is 0.71 but the decrease in log k_1 value for copper is 1.2. This abnormally large difference, assuming the validity of the above extrapolations, could be attributed to the steric hindrance offered by the benzene portion and the methyl group. If the benzene portion did not offer any steric effect the difference of log k_1 values

---

[15] J. T. Edsall, G. Felsenfeld, D. S. Goodman and F. R. N. Gurd, THIS JOURNAL, **76**, 3054 (1954).

[16] N. C. Li, J. M. White and E. Doody, *ibid.*, **76**, 6219 (1954).

for the benzimidazoles probably would be in the range of 0.4.

This unusual decrease in the stabilities with the benzimidazoles has not been exhibited in the study with cadmium. Since cadmium forms tetrahedral complexes, the steric effects would be at a minimum.

Nozaki[7] has studied the stereochemistry of the copper(II) complexes of imidazole and 4-methylimidazole. He concluded that the 4-coördinated complexes could not have a coplanar structure because of the marked overlapping of the van der Waals radii of the hydrogen atoms on adjacent imidazole molecules. Presumably, some or all the imidazole molecules must rotate around the Cu-N bond to give a puckered complex. This same type of reasoning could be applied to the present study with copper(II) and benzimidazole. Fisher–Taylor–Hirschfelder models show that the copper(II) complex could not exist in a coplanar form by any reasonable change in dimensions. The structure which gives the least steric interference would be the one which has two adjacent benzene rings of the benzimidazole molecules orientated down with the other two benzene rings orientated upwards. Figure 1 shows the two types of orientation of the benzimidazole molecules.

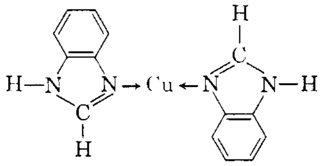


Fig. 1.—Orientation of the benzene molecule in the copper(II) complex.

The study of the stability constants of the 2-hydroxymethylbenzimidazole and 1-methyl-2-hydroxymethylbenzimidazole showed conclusively which of the two nitrogen atoms in the benzimidazole is coördinating. Basolo[17] has shown that a methyl group on the nitrogen atom of ethylenediamine decreases the stability of the complex even though the basicity of the chelating agent was increased. Results of the present study showed an increase in basicity and in chelate stability when the hydrogen atom in the 1-position of 2-hydroxymethylbenzimidazole is replaced by a methyl group. If coördination takes place through the nitrogen to which the methyl group is attached, a decrease in stability would be expected.

Acknowledgments.—The authors gratefully acknowledge financial aid from the Radiation Project of the University of Notre Dame supported in part under U. S. Atomic Energy Commission Contract AT (11-1)-38 and from a research grant A-2763 from the Department of Health, Education and Welfare, Public Health Service.

(17) F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 5243 (1952).

[Contribution from the Department of Chemistry, University of Notre Dame]

Stability Constants of Various Metal Ions with the 2-Hydroxymethylnaphthimidazoles[1]

By Thomas J. Lane, C.S.C., and Kenneth P. Quinlan[2]

Received June 8, 1959

The acid dissociation constants of 2-hydroxymethylnaphth[1,2]imidazole and 2-hydroxymethylnaphth[2,3]imidazole and the stability constants of their chelates with various metal ions have been determined in 50% aqueous dioxane by the potentiometric titration method. The preparations of the 2-hydroxymethylnaphthimidazoles by the Phillips method[3] are described. The 2-hydroxymethylnaphth[2,3]imidazole chelates of the divalent metal ions are more stable than the 1,2 isomer chelates. The difference is explained by the steric hindrance of the neighboring hydrogen atoms.

Introduction

In the preceding paper,[4] it was established that the chelation sites are the unsaturated nitrogen atom and the oxygen atom of the 2-hydroxymethylbenzimidazoles. As an extension of this work two compounds, Fig. 1, were chosen to show the steric effects of the ring system attached to the imidazole ring.

Experimental

Materials.—The dioxane was purified according to the method described by Vogel.[5] It was kept over sodium and distilled as needed.

Stock solutions of the metallic ions were prepared by dissolving the corresponding reagent grade perchlorates (G. Frederick Smith Co.) in water to approximately 0.01 *M*. In the case of lanthanum and cadmium, the nitrates (E. H. Sargent and Co.) were used. The metal ion stock solutions were standardized by the accepted methods of analysis.

Fisher reagent 0.1 *N* sodium hydroxide was standardized against Merck reagent grade potassium hydrogen phthalate. The 0.01 *N* perchloric acid was prepared from the Fisher 70% reagent grade acid. The perchloric acid was standardized against the sodium hydroxide.

2-Hydroxymethylnaphth[1,2]imidazole was originally prepared by Malmberg and Hamilton[6] by a fusion method. A modified procedure of the Phillips[3] method was used by us to prepare the compound. A mixture of 1,2-diaminonaphthalene (7.2 g., 0.043 mole), glycolic acid (3.6 g., 0.048 mole) and 185 ml. of 4 *N* hydrochloric acid was refluxed for 6 hr. A red-colored product was filtered from the cooled solution and dissolved in water. The 2-hydroxymethylnaphth[1,2]imidazole precipitated from the aqueous solution on the addition of sodium carbonate. The imidazole was washed free of the excess 1,2-diaminonaphthalene with a small quantity of acetone. After decolorization with charcoal and three recrystallizations from dioxane, the product was dried at 132° under vacuum for 3 hr. The pure product melted at 253–255° (dec.). The yield was 40%. This

---

(1) Presented before the Division of Physical Chemistry at the 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958.

(2) Abstracted from a thesis presented by Kenneth P. Quinlan in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(3) M. A. Phillips, *J. Chem. Soc.*, 2820 (1929).

(4) T. J. Lane and K. P. Quinlan, THIS JOURNAL, **82**, 2994 (1960).

(5) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 195.

(6) E. Malmberg and C. Hamilton, THIS JOURNAL, **70**, 2415 (1948).