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Steric effects on the formation constants of metal chelates of beta-diketones

Gerald Anthony Guter
Iowa State College

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STERIC EFFECTS ON THE FORMATION CONSTANTS
OF METAL CHELATES OF BETA-DIKETONES

by

Gerald A. Guter

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

Iowa State College

1955

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INTRODUCTION

Since the advent of the theoretical treatment of Bjerrum (1) on the measurement of formation constants and the application of this method to organic chelating agents very few systematic studies have been carried out in order to correlate steric requirements of ligands with their chelating abilities. It is the primary object of this study to contribute to the meager knowledge concerning steric effects in chelation from the vast field of theoretical organic chemistry where steric effects are quite well understood.

The recent widespread use of chelating agents as analytical reagents, their commercial application, and use as medicinals attest to the importance of increasing the theoretical knowledge of metal chelates. It is in this field that analytical chemistry searches for the specific, selective reagent. Although it was not anticipated at the beginning of this study that a selective reagent would be among the compounds studied the finding of one gives encouragement to future systematic studies in this field.

The chelating ability of the three beta-diketones was studied by means of their relative formation constants

in 75 percent dioxane. A definite trend was observed as the steric requirements of the chelating agent were increased. The steric effect manifests itself in three ways; (a) the separation factor becomes smaller for tetrahedral complexes; (b) for the square planar complex the formation constant becomes relatively smaller and the separation factor is large; (c) the relative solubilities in water and organic solvents and the difference in the ease of formation of the alkali metal chelates change markedly. A theory concerning the selectivity of dipivaloylmethane is given.

The work reported here should stimulate synthesis of selective reagents and systematic studies of this type.

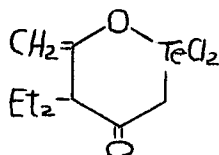
HISTORICAL REVIEW

Influence of Steric Hindrance on Chelation

Few systematic studies have been carried out with the purpose of correlating the steric requirements of ligands with their chelating properties. Among the first isolated instances which demonstrate the steric effect in chelation was a study by Morgan and Thomasson (2) who found that if the 3-position of acetylacetone was substituted with an isopropyl or secondary butyl group none of the usual colored copper and ferric chelates were formed. If a straight chain alkyl group was the substituent typical chelates were formed. This observation was the first to show the deviation in the properties of monoalkylated open chain diketones. Similar deviations had been noticed by Leser (3) who observed that 2-acetyl-dimethylcyclohexanone containing a branched chain substituted on the methylene group gave no copper chelate.

The study carried out by Morgan (2,4,5) pointed out that alkyl substituted acetylacetones which were substituted with branched chains at either the terminal carbon or central carbon atom were less capable of forming derivatives from tellurium tetrachloride than the unsubstituted diketone.

The tellurium complexes seemed to have very different properties than the chelates formed by other metals. The difficulty of their formation was not, however, attributed to a steric effect since 3, 3-diethylacetylacetone gave an excellent tellurium derivative and failed to give a ferric or copper chelate. Also the diketone anions were found as bivalent radicals in the condensations with selenium and tellurium tetrachlorides. In keeping with these facts the structure of the complex was proposed as



Similarly, 3-isopropylacetylacetone gave no reaction with cupric or ferric ions but readily gave the tellurium derivative.

The inability of 3-isopropylacetylacetone to chelate and the low formation constant of the 3-methylacetylacetone copper chelate was explained as a case of interference with the planar configuration of the chelate ring, which is necessary for complete resonance.

It has been well established that any substitution in the 2-position of 8-hydroxyquinoline prevents the precipitation of an aluminum complex. Irving, Butler, and Ring (7) concluded that the effect was due to the steric

hindrance provided by the group in the 2-position.

In order to further investigate the blocking effect of the 2-substituted 8-hydroxyquinolines Freiser et al. (8,9) determined the stabilities of several metal chelates of 2-methyl- and 2-phenyl-8-hydroxyquinoline. The metals used were Cu(II), Ni(II), Co(II), Zn(II), Mn(II), Pb(II), Cd(II), and Mg(II). The chelates of both 2-substituted 8-hydroxyquinoline has a less basic nitrogen atom than the corresponding 8-hydroxyquinolinates. Although 2-phenyl-8-hydroxyquinoline has a less basic nitrogen atom than the unsubstituted chelating agent Freiser attributes the lower stability of the 2-substituted chelates to some type of steric hindrance. This is justified since the 2-methyl group increases the basicity of the nitrogen toward protons and decreases the stability of the complex. It was also shown that the stability of the nickel chelates of these hindered agents was considerably less than would be expected or a larger steric effect was operating in the case of Ni(II) than the other metals. Freiser explains that this is so because Ni(II) has a tendency to form planar complexes and substitution at the 2-position would give rise to either a strained or distorted planar configuration or possibly even that of a tetrahedron.

A comparison of the ΔH° values obtained for these

reactions shows that where 2-substitution is involved the heats of chelation are only half that found associated with the respective chelates for the 4-methyl compound. It is thus reasonable to assume that the presence of the 2-methyl group prevents the close approach of the two ligands around the metal atom regardless of the preferred configuration. Freiser demonstrated that the magnitude of the steric effect increases with decreasing metal size by plotting the thermodynamic functions of the transchelation reaction where the 2-methyl-8-hydroxyquinoline anion is exchanged for the 4-methyl-8-hydroxyquinoline ligand. The plot reveals that $T\Delta S^\circ$ and ΔH° for the reaction are linear functions of the crystal radii of the metals, ΔH° for Ni(II) deviating considerably from linearity.

Another interesting point brought out in Freiser's data is that there is a much greater entropy increase for the formation of a hindered chelate. It was explained that the extra shielding of the 2-methyl group can more efficiently remove water molecules from the aquated metal ion. The decreased solvation would also help contribute to the smaller ΔH° value.

Freiser's explanation that Ni(II) has a tendency to form planar complexes should not pass without comment.

Martell and Calvin (10) point out that all compounds in which nickel is bound to four oxygen atoms, such as bis-acetylacetonate nickel, are paramagnetic. Mellor and Lockwood (11) have found that such chelates show considerable ionic character accompanied by considerable deviation of bond angles from the planar structure. If nickel is bonded either to nitrogen or to sulfur the diamagnetic or square planar structures are preferred.

Since the replacement of hydrogen atoms of ammonia by alkyl groups has a base strengthening effect, it is reasonable to assume that the strength of metal-amine complexes might be strengthened as well. This is the case with the silver-amine complexes which have been most extensively studied (12,13). Secondary amines give complexes of lower stability than would be expected from their proton basicity, and this effect is even more marked with tertiary aliphatic amines. The base strengthening effect of alkyl substitution is necessarily accompanied by an increase in molecular volume, and steric interference between amine molecules coordinated to a metal, and between amine molecules and solvated water, will tend to reduce the stability of such metal complexes.

It was not surprising to Irving and Griffiths (14) when they found that the N-alkylsubstituted ethylenediamines

showed decreasing ability to complex with Cu(II) even though the alkyl substituents increased the stability of the proton complex with the same ligands. This, of course, they attributed to steric factors. A portion of their data is presented here.

Table I

Stability Constants of
Copper(II) Complexes of N-alkylethylenediamines

Alkyl substituent	log K_1	log K_2	pK_{BH^+}
H	10.73	9.30	10.18
Methyl	10.55	8.56	10.40
Ethyl	10.19	8.38	10.56
<u>i</u> -Propyl	9.07	7.45	10.62

Although steric effects may be operating in this case, it is difficult to obtain a true evaluation unless the base strengthening effect of the alkyl substituent is first understood. In this case a comparison of formation constants with ligand basicity may not be justified. According to the views of Trotman-Dickenson (15) there is actually a greater difference between the basicities of primary and more highly substituted amines than the measurements obtained in water reveal. He suggests that

the greater solvation of ammonium ions than free amines makes the ammonium ions appear more stable when their dissociation constants are measured in water than when measured in an inert solvent. This stabilization increases with the number of protons in the amine cation, due to increased hydrogen bonding with the solvent.

Trotman-Dickenson was unable to obtain correlation between the catalytic coefficients of aniline bases for the decomposition of nitramide and their dissociation constants by one simple Bronsted equation. However, each class of amines given below obeyed a separate equation:

Tertiary amines	$k_c = 3.8 \times 10^{-5} K_a^{.64}$
Secondary amines	$k_c = 1.1 \times 10^{-5} K_a^{.64}$
Primary amines	$k_c = 4.1 \times 10^{-6} K_a^{.64}$

The three types of amines could be correlated by the same Bronsted equation if the dissociation constants measured in m-cresol were used. This led this worker to suggest that solvation effects in water lead to misunderstanding as to the true proton affinity of amines.

Unless these same solvation effects occur with metal amine complexes, the interpretation of free energy correlations with the pKa of the ligand is made only on unsound premises.

The type of steric effect observed by Irving and Griffiths (loc.cit.) may be classified as both the F and B strain described by Brown (16). The F or "frontal" strain acts between chelated ligand and solvent molecules around the mono-chelated metal. The B strain arises from the placement of three substituents plus a hydrogen atom on a single nitrogen atom and thus forces three of the normally tetrahedral bonds away from each other.

There are several other examples of steric inhibition to the formation of metal chelates (17). The foregoing have been singled out and they are the most systematic and the most complete studies.

Steric effects observed in chelation may be divided into the following three classes:

1. Steric requirements may influence the size of the chelate ring.
2. They may interfere with coplanarity of a chelate ring where resonance is possible.
3. Steric requirements may be large near the reaction site and thus interfere either directly with the metal bond or with other basic substances surrounding the metal such as solvating molecules.

The presence of a steric effect in any one class does not exclude its presence in another, and it is quite conceivable that 2 and 3 may occur frequently together.

The influence of the size of the chelate ring is quite well understood (18), five and six membered rings being the most stable due to decreased strain. Recently Irving et al. (19) have further discussed this effect in the light of Schwarzenbach's predictions concerning ring size and the chelate effect (20). Similarly the interference with the coplanarity of the ring has been widely discussed (21). At the present time Irving is carrying on investigations of this problem using 3,3'-substituted dipyridyls (22). This type of interference is also demonstrated by 3-substituted acetylacetonate where the central substituent will interfere with the terminal methyl groups and force the chelate ring out of planarity.

The following discussion will be centered about the third type of steric effect mentioned above. This type of steric effect does not have its parallel effects in other organic structures as the first two classifications seem to but rather is more related to effects found in sterically hindered Lewis acid-base reactions.

Correlations of Formation Constants with Basicities

Before searching for steric effects with the use of formation constants, a relationship between the strength of the chelate compound and more fundamental properties

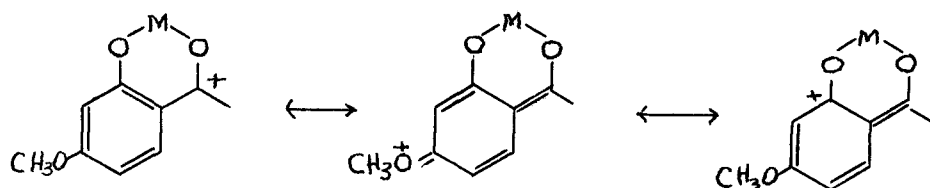
must be sought. It appears that there is no such single property to be found.

Calvin and Wilson (6) were the first to recognize the relationship between basic strengths of the ligands and formation constants of chelates. The group of compounds which was correlated contained substituted salicylaldehydes, naphthaldehydes, and beta-diketones. These compounds fell into at least two and probably four classes, each showing a linear relationship between the log formation constant for Cu(II) chelates and pKa of the chelating agent.

The analysis of this relationship indicated that both copper and hydrogen ions are bound partly by the same forces to the ligand and partly by different forces. The greatest difference according to them, and which accounted for the four separate groups, was the extent to which hydrogen and copper participate in the resonance of the chelate ring. This conclusion was drawn from the fact that each group of chelating agents involved chelate rings in which the bond order assigned to the carbon-carbon bonds was unique. In acetylacetone a bond order of 2 may be assigned, in salicylaldehyde 1.67, in 2-hydroxy-1-naphthaldehyde 1.5, in 2-hydroxy-3-naphthaldehyde 1.33. Resonance in the enol ring has been pointed out as one of the major

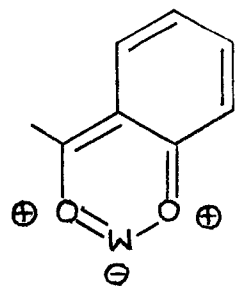
contributing factors to the stabilization of the enol form (23), and Calvin and Wilson argue that the bond order is a measure of the extent to which the chelate may participate in resonance structures such as those shown in Structures I to VIII.

There are intimations in the data of Calvin and Wilson which may help deciding the importance of Structures V and VI. Substitution of a methoxyl group in the four position of salicylaldehyde should provide additional stability to Structures III and IV by the electron releasing property of this substituent.

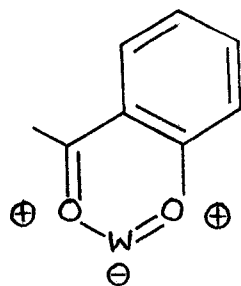


Thus the 4-methoxy group should greatly contribute to the stability of the chelate, actually this effect is observed. The 4-methoxysalicylaldehyde has a greater formation constant than the unsubstituted, or even the 3-methoxy compound, even though the basicity toward a proton is greater for the unsubstituted compound. The formation constants of the copper(II) chelates of these compounds are plotted against the Hammett sigma constants in Figure 1, and the large positive deviation of the 4-methoxy compound is clear.

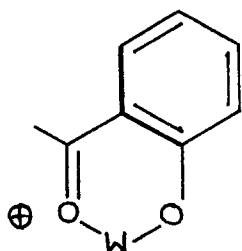
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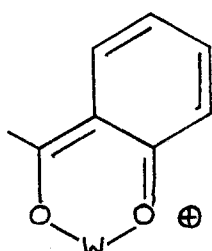
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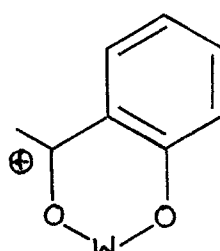
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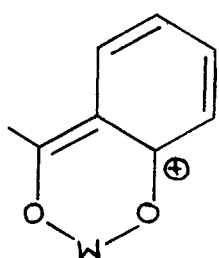
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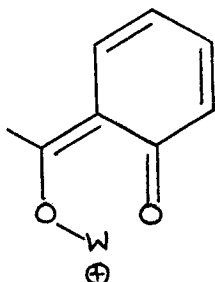
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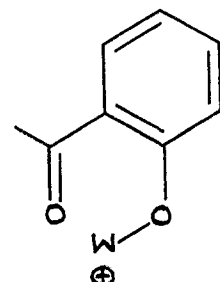
III



II



I



If the beta-diketones are considered next, a major deviation occurs in 3-methylacetylacetone exhibiting suppressed chelating properties. As is discussed on page 110 the enol form of 3-methylacetylacetone is hindered and does not allow planarity of the ring. The enol is thus thought to exist mainly in the acyclic form. Slight deviation may be accounted for because these two compounds are much less enolic than the others listed here.

A series of sixteen formation constants of beta-diketones has also been obtained for Cu(II) by Van Uitert (24). Excellent linear relationships have been obtained between these constants and the pKa of the chelating agent.

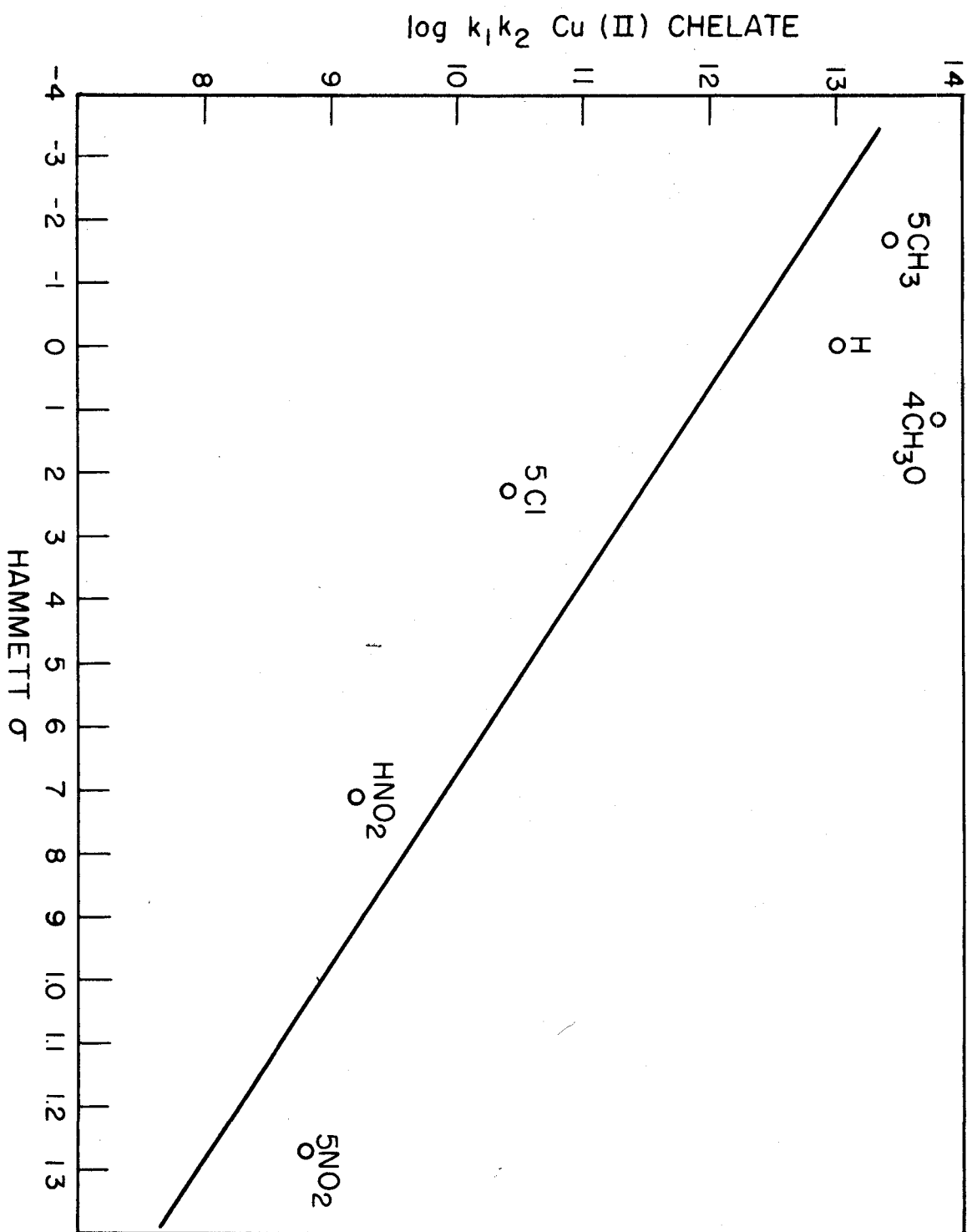
From the above correlations it is apparent that the two fundamental properties to which formation constants are related are the pKa of the reagent and a factor associated with resonance stabilization of the chelate ring.

In the remaining part of this section a model chelating agent is constructed at least in a qualitative fashion with the aid of new data taken from the literature as well as some previously given. The properties of more complex chelating agents are then inferred from those of the model, especially where non-conformity is observed, so that later steric effects may be better evaluated.

Figure 1

Correlation between Hammett sigma and
Formation Constants of Substituted Salicylaldehydes

The sigma constants used are those meta or para to
the hydroxide group.



Recently, complex ion equilibria have been correlated on a double basicity scale by Edwards (25). The correlation of 108 formation constants is made on the basis of the equation

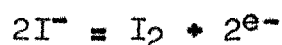
$$\log \frac{k}{K_0} = \alpha E_n + \beta H$$

where k/K_0 is a relative (to water) rate or equilibrium constant and E_n is a nucleophilic constant characteristic of the ligand. H is the relative basicity of the donor to protons, and α and β are substrate constants, characteristic, in this case, of the metal ion. By definition

$$H = pK_a + 1.74$$

$$E_n = E^0 + 2.60$$

where E^0 is the electrode potential given by Latimer for oxidative dimerizations of the type



Although formation constants of metal chelates are not correlated by Edwards those correlations which involve metal ions and monodentate ligands such as ammonia, pyridine, phenoxide ion, or any monodentate group which could be incorporated into a polychelating agent may possibly serve a useful purpose. This type of correlation appears to be a

step forward from the previously discussed correlation where a double basicity scale was intimated.

It is useful to observe the fundamental relationship between the Hammett rho sigma correlations (26) and those of Edwards. When considering formation constants of the type



where A_o and A are anions of benzoic acid and substituted benzoic acids respectively, the Hammett correlation demands the following relationship:

$$\log \frac{k}{k_o} = \rho \sigma$$

where k is the equilibrium constant for reaction (1) and k_o is the equilibrium constant for reaction (2), rho is a reaction constant and sigma is a constant characteristic of the meta or para substituent in A .

According to the Edwards correlation the following relationships would hold:

$$\log \frac{k}{K_o} = \alpha E_n + \beta (pK_a + 1.74)$$

$$\log \frac{k_o}{K_o} = \alpha E_{n_o} + \beta (pK_{a_o} + 1.74)$$

then
$$\log \frac{k}{k_0} = \alpha(E_n - E_{n_0}) + \beta(pK_a - pK_{a_0})^*$$

Comparing this with the Hammett relationship it is found that

$$E_n = E_{n_0}$$

$$\beta = \rho$$

This appears to be a necessary condition for conformity to the Hammett equation. It is entirely possible that substituents capable of distributing the electronic charges over a wider area are capable of influencing E_n and produce deviations from the ρ α treatment. Furthermore, it is shown by the values of E_n and H given by Edwards that no dependent relationship exists between them. Thus, any linearity found between formation constants and pK_a cannot be a result of the linear dependence of $(E_n - E_{n_0})$ upon pK_a . Deviations for complex ion equilibria would be expected to be larger than for carbon displacement

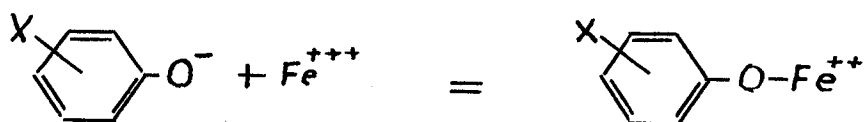
*This implies a perfect fit of the Edwards equation. There is the possibility that when the Hammett equation breaks down the Edwards equation will also break down implying a relationship such as

$$\log \frac{k}{K_0} = \alpha E_n + \beta H + f(q)$$

where q are other molecular parameters.

reactions, since the α values are much larger for the metal ion substrates.

Data to test the relationship between Hammett and Edwards treatments have been presented by Milburn (27). It was found that equilibrium constants for the reaction



where X = *p*-CH₃, H, *p*-Br, *m*-Br, and *p*-NO₂ showed a scattering of points for the Hammett plot which was greater than expected from the random errors. The deviations of points were about ten times the average standard deviation in log formation constant. Milburn suggests that the scatter could be accounted for by potential energy terms of a type not operative for the acid dissociation, for example, the O-Fe bond could have some double bond character.

The data are replotted in Figure 2, and a slope required by the Edwards equation (0.56) is drawn. Any large deviations must be due to large differences in En. It is noted that the *p*-NO₂ compound decreases the complex stability more than that predicted. If double bonding for the O-Fe bond is important a *p*-NO₂ group would decrease the complex stability by its electron withdrawing properties.

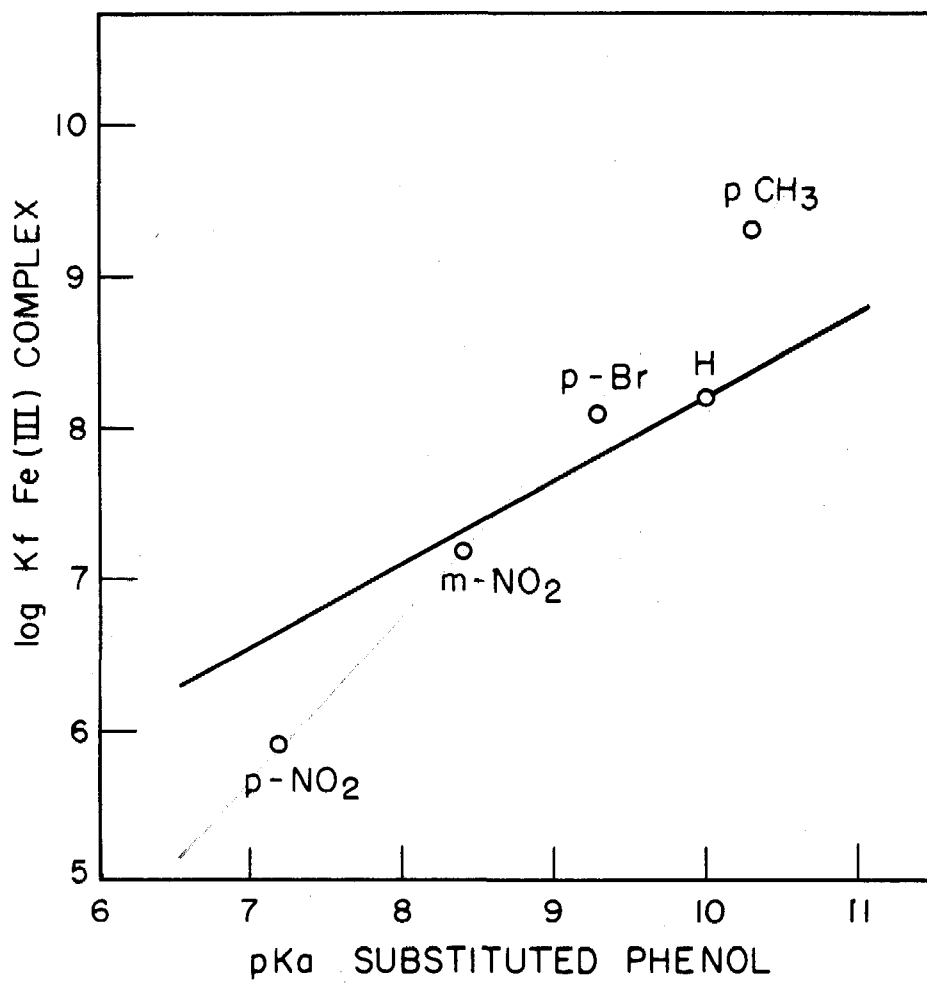
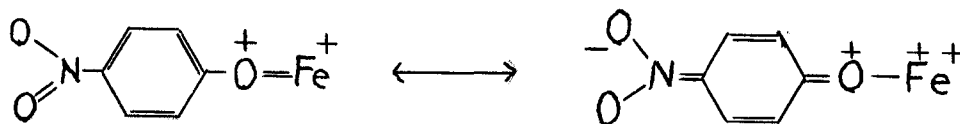


Figure 2

Correlation Predicted by Edwards Equation



When reactions of the type



were correlated by Edwards, it was found that for Cu(II)

$$\alpha = 4.69$$

$$\beta = .958$$

That the formation constants of Cu(II) chelates are not correlated by this equation is shown by the predicted slope of $d \log K_{(\text{chel})} / dpK_a = 0.958$. Calvin and Wilson (loc.cit.) show that this slope is 1.71, nearly twice that predicted by the Edwards equation. This is understood since the chelate effect would enhance the basicity of the ligands if they are in the form of a bidentate ligand.

The above facts suggest the following:

- a. Where substitution on the ligand is involved in some cases it is possible to vary the pKa of the nucleophile without changing the En values.
- b. For a group of chelating agents where the pKa varies with substitution the chelate effect remains constant, i.e.

$$\log k(\text{chel}) = \underline{X} \log k_f + \underline{x} \quad (\text{II})$$

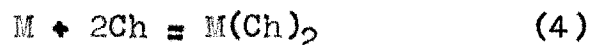
where

$$\log k(\text{chel}) = \log \frac{\overline{M}(\text{Ch})_2}{\overline{M} \overline{\text{Ch}}^2}$$

$$\log k_f = \log \frac{\overline{M} B_4}{\overline{M} \overline{B}^4}$$

Where Ch is a chelating agent and B is a similar monodentate group, and the large and small chi's are constants associated with the chelate effect.

The (b) assumption requires a linear free energy relationship between the reactions



Appropriate examples would be where the B's are substituted pyridines and the Ch's are correspondingly substituted bipyridyls formed by joining two B groups together.

Irving et al. (28) have shown that such a linear relationship exists when the metal ion is varied from Co(II) to Ni(II) to Cu(II) and the first chelate effect, $\text{chel}(I)$, for ethylenediamine is

$$\text{chel}(I) = \frac{\log K_1(\text{en})}{K_1 K_2 \text{NH}_3} = 0.20 \log K_1 K_2 \text{NH}_3 + 1.40$$

and

$$\text{chel(II)} = \frac{\log K_2(\text{en})}{K_3 K_4 (\text{NH}_3)} = 0.32 \log K_3 K_4 (\text{NH}_3) + 2.43$$

and found the chel(I) and chel(II) diminished as the number of methylene groups between the terminal groups increased.

It is apparent that the chelate effect constants will depend on the following:

1. The metal ion involved.
2. The size of the chelate ring formed.
3. Whether or not the bidentate ligands assume a different configuration about the metal atom than the monodentate ligands.
4. Whether or not a resonance stabilized chelate ring is formed.
5. The number of bridges between the monodentate groups.

According to the validity of assumptions (a) and (b) the formation constant for the chelating agent may thus be expressed by combining the Edwards equation with (II), so that

$$\log K_{\text{chel}} = \sum \beta pK_a + \sum \alpha (\text{En} + 1.74\beta) + \log K_0 + \sum \gamma \quad (\text{III})$$

where pK_a and En are properties of a monodentate group and are probably directly related to those of a similarly

constituted bidentate ligand. The evaluation of X and the relationship between pK_a of a bi- and monodentate ligand should thus give the slope of the linear relationship, since all the bracketed terms are constant for similar ligands.

That a linear relationship would exist between reaction (3) and (4) may be arrived at by considering the Hammett plots for each of these two reactions. If reaction (3) involved Cu(II) and substituted pyridines we may expect this set of equilibrium constants to give the Hammett plot. If reaction (4) involved Cu(II) and substituted bipyridines a similar Hammett relationship would be expected. The $\log K_3$ and $\log K_4$ which are separately linear with the sigma values are thus linear with each other. The linear relationship thus expected for (3) and (4) must obey all restrictions placed on the Hammett relationship.

A comparison of the para sigma values and the formation constants of 5-substituted-1,10-phenanthrolines (29) shows excellent agreement and supports the view that such agreement would also be found in bipyridines as well as pyridines. In fact, reaction (4) might just as well involve 1,10-phenanthrolines.

Table II

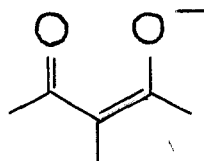
Correlation between
Formation and sigma Constants

1,10-Phenanthroline substituent	pKa	log(chel)	$m \sigma$	$p \sigma$
5-CH ₃	5.23	22.3	-.069	-.170
5-H	4.95	21.3	0	0
5-Cl	4.26	19.7	+.373	+.227
5-NO ₂	3.57	17.8	+.710	+.778
2,2'-Bipyridine	4.35	17.8		

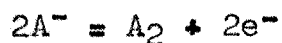
The relationship (III) would correlate only a small number of chelating agents with the properties of simpler monodentate ligands and a chelate effect. Most chelating agents are not only unsymmetrical but cannot be considered as being built from a pair of monodentate ligands and the properties of the "semi" bidentate ligand are nonexistent. However, it may be argued by analogy that the materials from which a chelate formation constant is built are common to all chelates and (III) merely expresses these factors in terms of simpler ligands, and may be translated into the terms of more complex ligands.

Salicylaldehydes and beta-diketones are examples of complex ligands, but the work of Calvin and Wilson (loc.cit.)

indicate $\log K(\text{chel})$ against pK_a gives the same slope for each series of compounds but different intercepts. This, of course, is interpreted in terms of (III) that $\underline{X} \beta$ is the same for each class or may be considered common for the group:



Different E_n values may account for the different intercepts. Whether the electrons of the ring are made available for the reaction



or for participation in resonance these two explanations appear to be one in the same.

It was pointed out by Brandt and Wright (29) that bipyridyl did not follow the same relationship between \log chelate constants and pK_a of 1,10-phenanthrolines, with bipyridyl giving a less stable chelate than is expected from the pK_a (see table on page 27). This deviation may be explained by considering the free energy changes involved in the two reactions





In the free energy expression for the second reaction partition functions for rotation and vibration associated with the bond connecting the two rings are greatly diminished, however, in the products they appear to be about equal. This means a more positive entropy change for the second reaction and hence a tendency toward stabilization of the metal chelate. This would be reflected in the χ values of equation (III) since it would bear directly on the free energy relationship required by \bar{X} and \underline{x} . It is unfortunate that suitably substituted bipyridyls are not available to further clarify this effect.

Van Uitert, Fernelius, and Douglas (30) have made a study of the effect of various end groups on the chelating properties of beta-diketones. They have found that the formation constants fall into three linear relationships with pK_a of the ligand, each class unique in the number of ring end groups on the beta-diketones. Those containing methyl end groups have smaller chelating ability than a beta-diketone which has two ring systems as end groups. The data in Table III show this and the type of end groups involved.

Table III

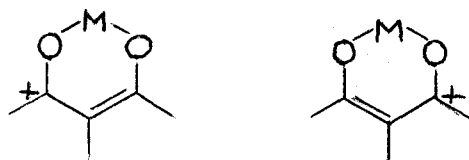
Formation Constants of beta-Diketones

Compound	pKa	log $K_{Cu(chel)}$	
2-Thenoylbenzoylmethane	13.50	12.28	11.42
Dibenzoylmethane	13.75	12.98	12.00
2-Furoylbenzoylmethane	12.95	12.48	11.44
Di-2-thenoylmethane	12.63	12.23	11.28
2-Thenoyl-2-furoylmethane	12.30	11.92	10.01
Benzoylacetone	12.85	12.05	10.96
Acetylacetone	12.70	11.85	10.74
2-Thenoylacetone	12.35	11.70	10.68

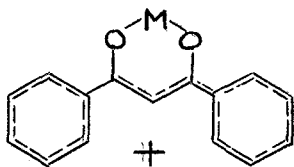
The explanation given for this effect was that apparently a steric factor is operating. The methyl group is less effective than a ring group in shielding the metal ion from external contacts with the solvent. This explanation is not reasonable since the bulkier ring would also have more difficulty attaching itself to the metal by excluding more solvent from the metal atom.

An alternative explanation may be given. From the plot of log $K(chel)$ against pKa two (and possible three) straight lines are obtained with each line corresponding to the number of ring end groups present. In terms of

the modified Edwards equation this is interpretable on the basis of differing polarizabilities. That this property may differ from acetylacetone to dibenzoylmethane and may be revealed by considering the structures



If these structures are important, phenyl groups on the one and three positions may greatly contribute to the stability of the chelate by structures such as

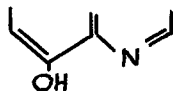


Furyl and thenyl groups would have the same effect.

Irving and Rossotti (33) have reached the conclusion that the linear relationship between chelate constants and pK_a will deviate when steric effects are involved. This is a result of their investigations on "the thermodynamic derivation of this and related equations (which) will be published shortly". Some of their conclusions are that for a given metal and a series of ligands of similar type the plot of $\log K_1(\text{chel})$ against pK_a should be a straight line of unit slope; major deviations will occur when steric effects are involved and $\log K_1(\text{chel})$ will always be much

smaller than predicted; minor deviations where $\log K_1(\text{chel})$ will be either slightly larger or smaller may also occur.

These authors present data which show that when substitution near the functional group



occurs a change in the formation constant can be accounted for by steric or inductive effects which alter the basicity of either the oxygen or nitrogen. The compounds which deviated considerably from the predicted line of unit slope from the magnesium complexes were 8-hydroxy-7-methylquinoline, 8-hydroxy-2-methylquinoline, 8-hydroxy-2,4-dimethylquinazoline, and 8-hydroxy-4-methyl-2-phenylquinazoline.

Some confusion may result from these authors' treatment of the data. The pKa of the OH group was taken as a measure of the proton affinity for the entire molecule. This, for the 8-hydroxy-2-methylquinoline the inductive effect of the methyl group increases the proton affinity of the nitrogen. The variable nitrogen basicity might just as well be included to avoid missing small steric effects.

Irving and Rossetti also argue that if, for a

given cation, the stability of the complex depended only on the strength of the corresponding ligand-hydrogen bond then a plot of $\log K_{\text{chel}}(\text{A})$ against $\log K_{\text{chel}}(\text{B})$ for a series of cations should give a straight line of unit slope and of intercept equals $\text{pKa}(\text{A}) - \text{pKa}(\text{B})$, and they attribute departures from this linearity of unit slope and theoretical intercept to steric and other factors. Constants which demonstrated this linearity were $\log K_1$ for the Mg(II), Zn(II), Ni(II), $\text{UO}_2(\text{II})$, and Cu(II) chelates of 8-hydroxyquinoline and $\log K_1$ for the corresponding metal chelates of 8-hydroxy-5-methylquinoline. When the corresponding constants for 8-hydroxycinnoline and 8-hydroxy-2-methylquinoline were plotted against the parent compound serious deviations were noted. In the case of 8-hydroxy-2-methylquinoline deviations were attributed to steric interference of the methyl groups. In the case of 8-hydroxycinnoline only the constant for the Mg(II) complex fell on the theoretical line, and deviations became more serious as stability of the complexes increased. The authors attribute these deviations to "specific behavior" due to the low value of pK_{NH} for 8-hydroxycinnoline. It was pointed out that this would be expected to reduce the stability of the Cu(II) complex and similar metals and have little or no effect on the Mg(II) complex.

According to the modified Edwards equation, the $\log K_{\text{chel}}$ constants of two different ligands A and B and a series of metals may be treated as follows:

$$\log K_{\text{chel}(A)} = \frac{\alpha}{\beta} pK_{a(A)} + \frac{\alpha}{\beta} \text{En}_{(A)} + 1.74 \frac{\alpha}{\beta} \\ + \log K_o + \alpha$$

$$\log K_{\text{chel}(B)} = \frac{\alpha}{\beta} pK_{a(B)} + \frac{\alpha}{\beta} \text{En}_{(B)} + 1.74 \frac{\alpha}{\beta} \\ + \log K_o + \alpha$$

If chelate A and B are similar so that $\text{En}_{(A)}$ equals $\text{En}_{(B)}$ but differ greatly in pK_a , then for any given metal

$$\log K_{\text{chel}(A)} = \log K_{\text{chel}(B)} + \frac{\alpha}{\beta} (pK_{a(A)} - pK_{a(B)})$$

This equation is in partial agreement with the statement of Irving only if beta is constant for all metals or if

$$pK_{a(A)} = pK_{a(B)}$$

When the basicities of two ligands are equal or nearly so, a plot of $\log K_{\text{chel}(A)}$ against $\log K_{\text{chel}(B)}$ will be a straight line of unit slope. This is true in the case of 8-hydroxy-2-methylquinoline and 8-hydroxy-5-methylquinoline where ΔpK_a as given by Irving is +0.31. Unless $\frac{\alpha}{\beta}$ is very large deviations from predicted linearity will be small or unnoticed. The 8-hydroxy-

cinnoline complexes, however, do show deviations. In this case ΔpK_a is -1.96 where the \underline{X} $\underline{\beta}$ coefficients become important, and deviations due to varying either \underline{X} or $\underline{\beta}$ may show up here. The only two metals in Irving's study which have been assigned $\underline{\beta}$ values are ZnX_4 and CuX_4 being 0.650 and 0.958 respectively. On this basis it is understandable why Irving found Cu(II) complexes to give greater deviation than Zn(II) complexes.

Similar deviations were found for the chelating agents listed in Table IV. The ΔpK_a refers to the difference between these reagents and 8-hydroxyquinoline.

Table IV

Correlations of
Formation Constants of Oxines

Compound	ΔpK_a	Deviations
8-hydroxy-2-methylquinoline	+0.21	yes
8-hydroxy-5-methylquinoline	+0.30	no
8-hydroxycinnoline	-1.96	yes
8-hydroxyquinazoline	-1.21	yes
5-hydroxyquinoxaline	-1.51	yes
8-hydroxy-4-methylcinnoline	-1.80	yes

EXPERIMENTAL

Preparation of Materials

Preparation of beta-diketones

Diisobutyrylmethane and dipivaloylmethane (DPM) were prepared by condensing the appropriate ester and ketone using sodamide as the condensing agent according to the procedure of Hauser and Adams (31).

Dipivaloylmethane was identified by the melting point of its Cu(II) chelate 190 to 191^o*. The fraction of the liquid boiling 94.0 to 94.5^o 20 mm. was saved after distillation through a center rod column. Diisobutyrylmethane which was not previously prepared by this method gave a Cu(II) chelate melting 127 to 129^o. The fraction boiling at 80.5 to 81.4 at 17mm. was saved.

Anal. Calcd. for C₉H₁₆O₂: C 69.21; H, 10.32.

Found: C, 69.5; H, 10.2.

Acetylacetone (Eastman Kodak Co.) was purified by fractionation. The middle fraction boiling at 127^o was used in all cases.

*All melting points and boiling points in this section are uncorrected.

3-Methylacetylacetone was prepared by acid catalized condensation of acetic anhydride with ethylmethylketone according to the procedure of Hauser (32). The fraction boiling 75.0° at 30 mm. was used for infrared, and ultra-violet absorption measurements.

Preparation of reagents

Dioxane was purified by refluxing with dilute hydrochloric acid, drying over potassium hydroxide and flash distilled from sodium metal according to the procedure used by Calvin and Wilson (6). It was fractionated immediately before use.

Standard potassium hydroxide in mixed solvents. The most convenient method for preparing carbonate free base without introducing foreign materials such as barium chloride or base exchange resins was by adding clean pieces of potassium metal (about two grams) to a bottle containing 750 ml. of pure dioxane under a nitrogen atmosphere. The bottle was then sealed with a stopper equipped with nitrogen inlet and outlet and a small addition funnel. Water was cautiously added to the dioxane as nitrogen passed through the system. After the potassium metal had all dissolved enough water was added to give the solvent the desired percentage. Vigorous shaking was usually

required to form a homogeneous solution. The solution was then stored under nitrogen.

Potassium perchlorate which was used as the inert electrolyte in the potentiometric titrations was reagent grade, but it was found necessary to recrystallize it from water at least once to free it of undesirable acidic components.

Metal perchlorates were reagent grade (G. F. Smith). Stock solutions were prepared of approximately 0.0125 molar.

Infrared and Ultraviolet Spectra

Infrared absorption spectra

Pure liquids of acetylacetone, diisobutyrylmethane, dipivaloylmethane, and 3-methylacetylacetone were used in a capillary cell on a Baird spectrophotometer. These spectra are shown in Figures 3 and 4. The liquids were used without further purification. Samples of dipivaloylmethane were also used to obtain high resolution spectra in the 3 to 5 micron region using the Perkin Elmer Model 13 with lithium fluoride prisms. This and other high resolution spectra including the copper chelate of DPM are reproduced in Figure 5.

Figure 3

#5515 -- Acetylacetone

#5514 -- 3-Methylacetylacetone

#5510 -- Diisobutyrylmethane

I.B. SPECTROPHOTOMETER	
NO.	5515
DATE	NOV 1951
NAME	Shelvis
LABORATORY	Research Division
Ca ²⁺ -Ox ²⁻ salt	
E.M. G. & B. Co.	
MANUFACTURER	EMERY
MODEL	5515
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS

I.B. SPECTROPHOTOMETER
NO. 5515
DATE NOV 1951
NAME Shelvis
LABORATORY Research Division
Part of work of Shelvis

I.B. SPECTROPHOTOMETER	
NO.	5514
DATE	NOV 1951
NAME	Shelvis
LABORATORY	Research Division
Part of work of Shelvis	
E.M. G. & B. Co.	
MANUFACTURER	EMERY
MODEL	5514
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS

I.B. SPECTROPHOTOMETER
NO. 5514
DATE NOV 1951
NAME Shelvis
LABORATORY Research Division
Part of work of Shelvis

I.B. SPECTROPHOTOMETER	
NO.	5513
DATE	NOV 1951
NAME	Shelvis
LABORATORY	Research Division
Part of work of Shelvis	
E.M. G. & B. Co.	
MANUFACTURER	EMERY
MODEL	5513
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS
WAVELENGTH RANGE	2.5-15.0 MICRONS
WAVELENGTH	10.0 MICRONS

I.B. SPECTROPHOTOMETER
NO. 5513
DATE NOV 1951
NAME Shelvis
LABORATORY Research Division
Part of work of Shelvis

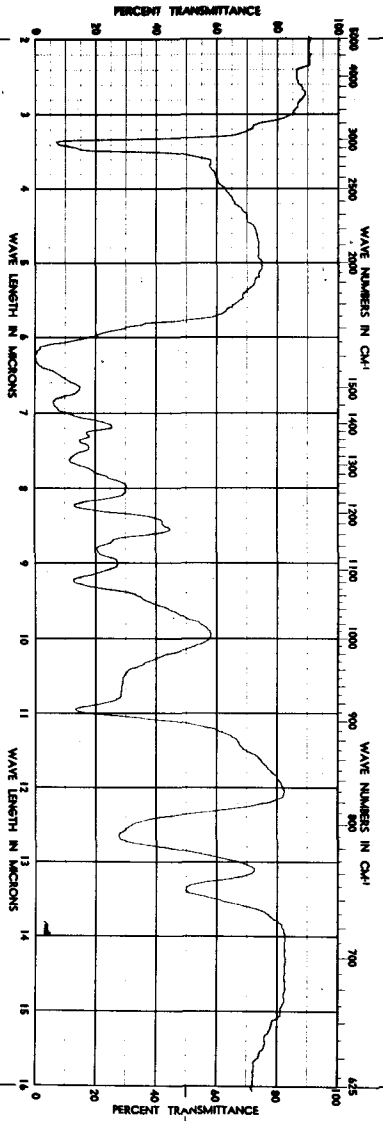
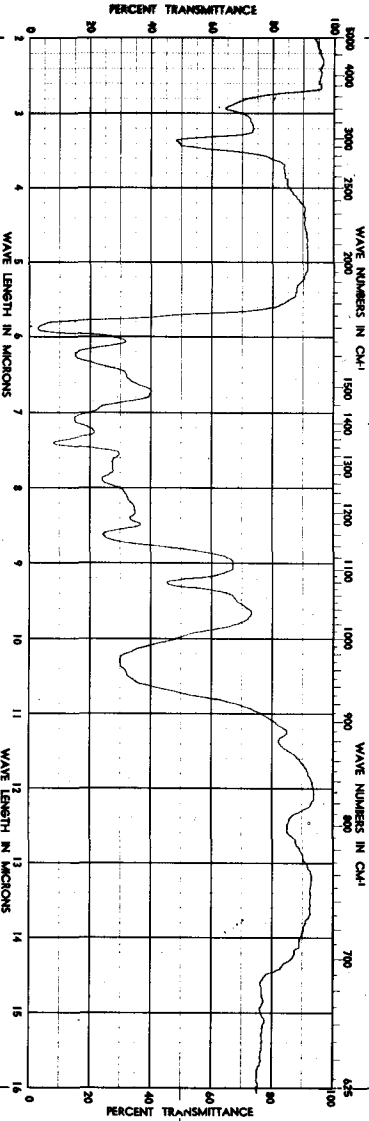
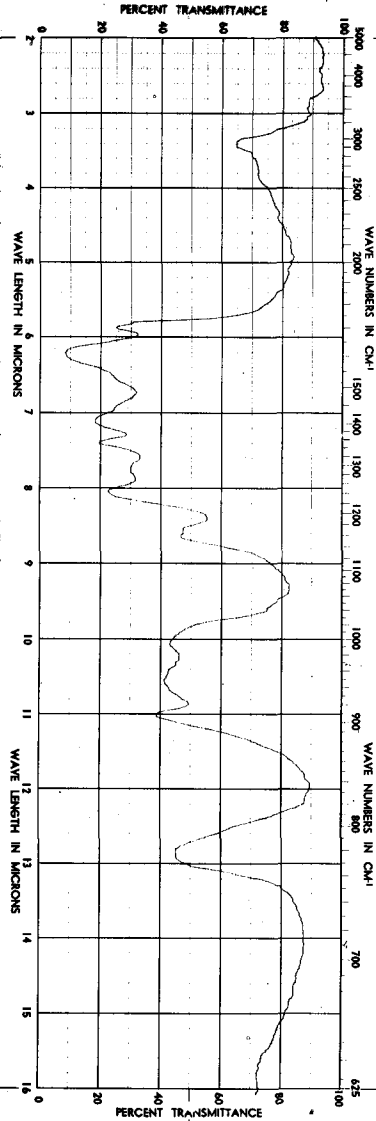


Figure 4

#5917 -- Dipivaloylmethane

#6100 -- Lithium Chelate of Dipivaloylmethane

#7360 -- Deuterated Acetylacetone

I.R. SPECTROPHOTOMETER
 NO. 5317
 DATE 1-20-57
 NAME S. G. G. G.
 SAMPLE Diethylmethane
 FROM C. G. G. G.
 SAMPLE CELL MM CHK.
 REF. CELL MM CHK.
 CELL MS. MS.
 SOLV. *Diethylmethane*
 VOL. CC. % CC. %
 FILTER C. G. G. G.
 I.R. SPECTROPHOTOMETER
 PERKIN-ELMER, INC.
 CAMDEN, NEW JERSEY, U.S.A.

I.R. SPECTROPHOTOMETER
 NO. 5100
 DATE 1-20-57
 NAME S. G. G. G.
 SAMPLE Diethylmethane
 FROM C. G. G. G.
 SAMPLE CELL MM CHK.
 REF. CELL MM CHK.
 CELL MS. MS.
 SOLV. *Diethylmethane*
 VOL. CC. % CC. %
 FILTER C. G. G. G.
 I.R. SPECTROPHOTOMETER
 PERKIN-ELMER, INC.
 CAMDEN, NEW JERSEY, U.S.A.

I.R. SPECTROPHOTOMETER
 NO. 7350
 DATE 1-20-57
 NAME S. G. G. G.
 SAMPLE Diethylmethane
 FROM C. G. G. G.
 SAMPLE CELL MM CHK.
 REF. CELL MM CHK.
 CELL MS. MS.
 SOLV. *Diethylmethane*
 VOL. CC. % CC. %
 FILTER C. G. G. G.
 I.R. SPECTROPHOTOMETER
 PERKIN-ELMER, INC.
 CAMDEN, NEW JERSEY, U.S.A.

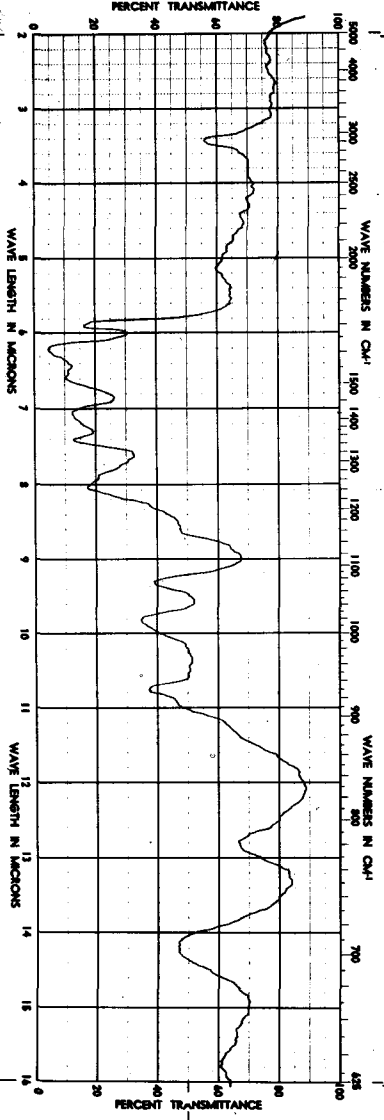
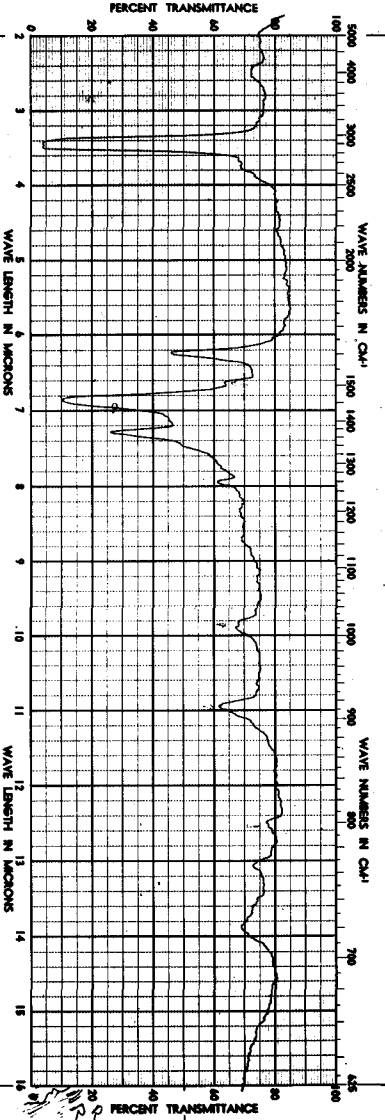
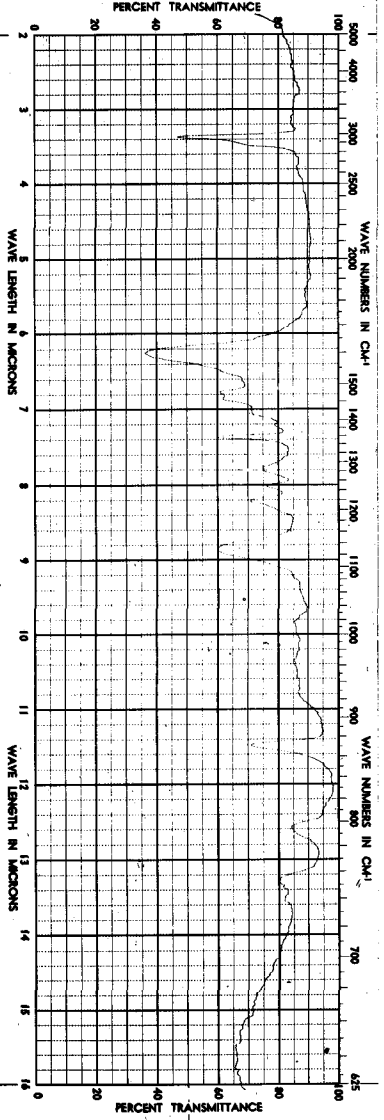
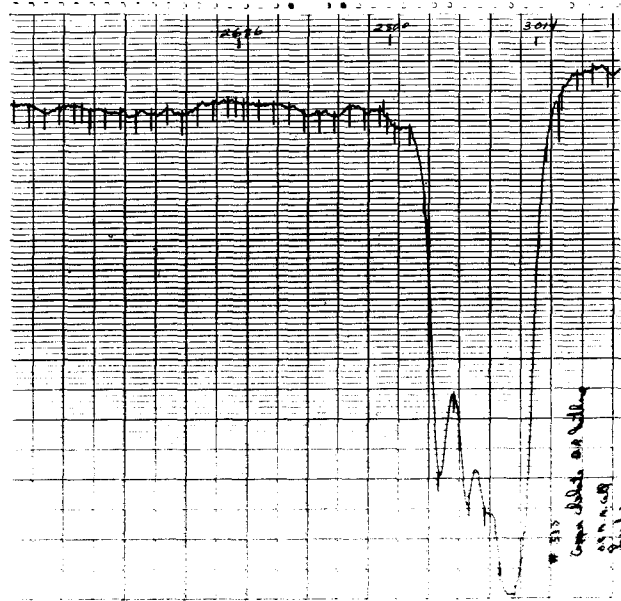
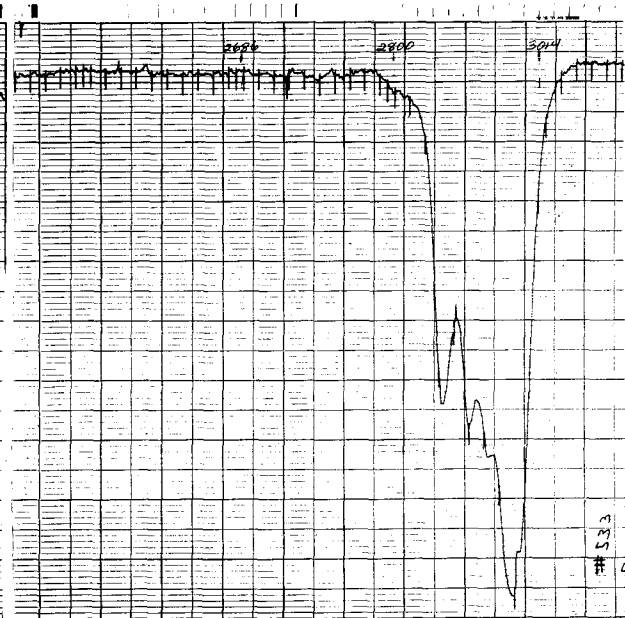
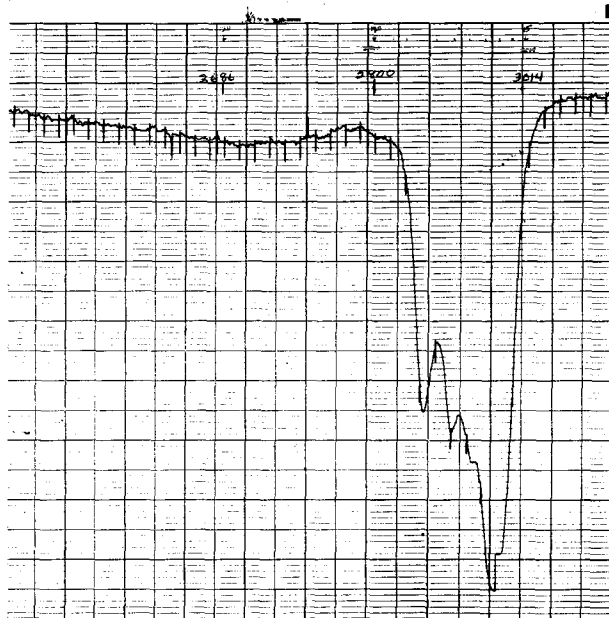


Figure 5

Dipivaloylmethane

Deuterated Dipivaloylmethane

Copper Chelate of Dipivaloylmethane



Deuterated samples of acetylacetone and dipivaloylmethane were prepared by the ion exchange method. The acetylacetone was dissolved in sodium deuterioxide solution which was then acidified with deuterio sulfuric acid. The acetylacetone which separated from the aqueous layer was removed and dried over calcium chloride. Since the sodium salt of dipivaloylmethane was insoluble in the basic solution it was dissolved in ether and shaken with this solution. The ether solution was then separated and shaken with deuterio sulfuric acid solution. The ether was dried and evaporated from the deuterated dipivaloylmethane which was then fractionated. The spectras are shown in Figure 2. Samples of acetylacetone and dipivaloylmethane were treated in the same way as described above except sodium hydroxide and sulfuric acid were used. Infrared spectra were found to be identical with those previously taken on the undeuterated compounds.

Lithium chelate of dipivaloylmethane was prepared by shaking a 0.1N solution of DPM in ether with a 2N solution of lithium hydroxide. The solutions were separated and evaporation of the ether yielded white chelate. A sample was used to obtain the infrared spectrum given in Figure 4 without further purification.

Ultraviolet absorption spectra

All were taken with a Beckman model DU spectrophotometer with the cell compartment thermostated at 25°. Square one cm. cells were usually used except when it was necessary to keep the solution in the cell for long periods of time, in which case the one cm. cylindrical cells were used.

Cyclohexane and acetonitrile were the only two solvents used which required purification by distillation. Isooctane (Phillips) and absolute ethanol required no purification. The water used was "de-ionized" through an ion exchange column (Barnstead Bantam).

The absorption curves are summarized in Table V. The solutions were prepared by accurately weighing out 1×10^{-3} moles of the purified compounds and dissolving them to form 100 ml. of solution. This solution was then diluted one hundred fold to obtain solutions which absorbed in the range of the spectrophotometer. When water solutions of diisobutyrylmethane or dipivaloylmethane were required a stock solution of ethanol was diluted one hundred fold with water.

Table V

Ultraviolet Absorption of beta-Diketones

Compound	Solvent	Max. (m μ)	Extinction coefficient
Acetylacetone	Acetonitrile	273	0.63×10^4
Acetylacetone	Isooctane	271	0.99×10^4
Acetylacetone	Water	274	0.15×10^4
Acetylacetone	NaOHaq.	294	2×10^4
Diisobutyrylmethane	Acetonitrile	274	0.71×10^4
Diisobutyrylmethane	Cyclohexane	274	1.11×10^4
Diisobutyrylmethane	Water	274	0.16×10^4
Dipivaloylmethane	Acetonitrile	276	1.09×10^4
Dipivaloylmethane	Isooctane	274	1.27×10^4
Dipivaloylmethane	Excess NaOH	294	1.81×10^4
Dipivaloylmethane	Water	278	0.18×10^4

Kinetics of Equilibration

The absorbances at the peaks of the ultraviolet spectra were compared with the known percent of enol content for each solvent. A direct relationship was observed as shown in Table VI. This data is plotted in Figure 6.

Stock solutions of the diketones were prepared in ethanol with a concentration of 1×10^2 molar. One ml. of

Table VI

Absorbance of Acetylacetone and Enol Content

Solvent	Absorbance of 1×10^{-4} m. solution	% Enol
Water	0.150	15.5 (34)
Acetonitrile	0.600	58 (35)
Chloroform	0.900	78 (35)
Cyclohexane	1.010	91 (34)

a stock solution was added to water which had been brought to 25° and the resulting solution was diluted to 100 ml. A sample of this diluted solution was rapidly placed in a quartz cell and inserted in the thermostated cell compartment of the spectrophotometer. The spectrophotometer had been previously balanced at the wavelength of the peak of the particular compound. The absorbance at this wavelength was then read at convenient time intervals. In the case of acetylacetone the operations had to be performed very rapidly and a habit formed before enough data could be obtained from a single run. The data was treated as follows:

A = Absorbance at enol peak

ϵ = Extinction coefficient of enol form

E = Concentration of enol form

K = Concentration of keto form

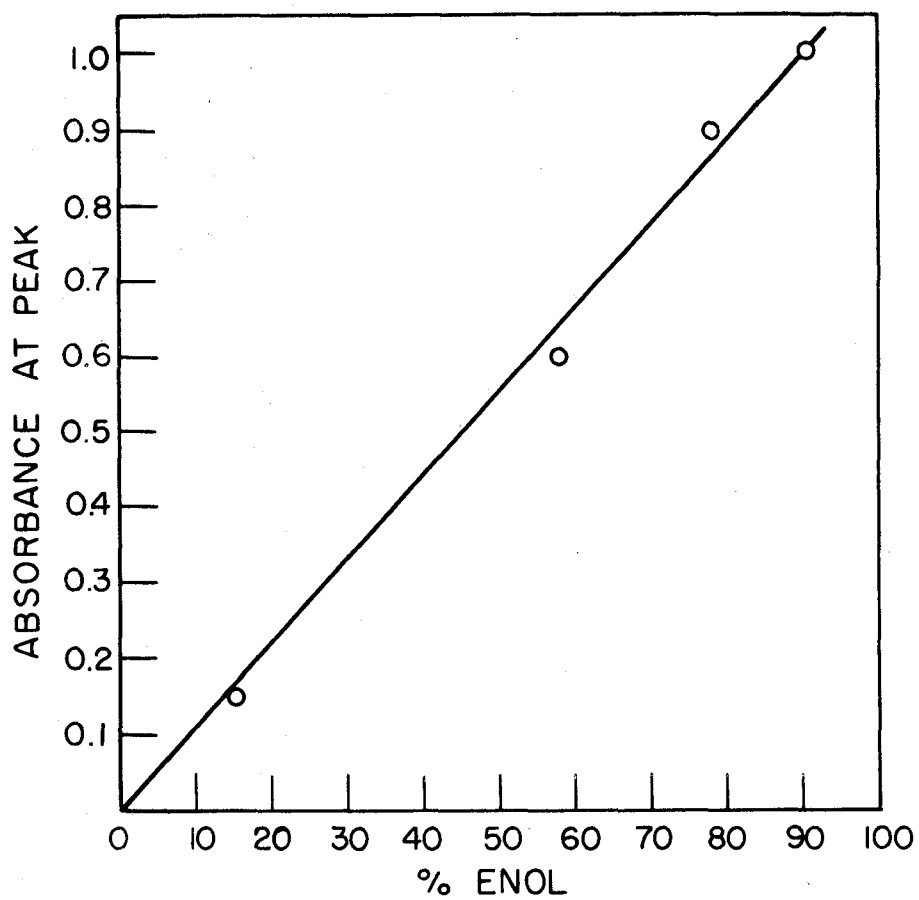


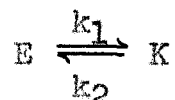
Figure 6

Comparison of Spectrophotometric
Data with Known Enol Content of Acetylacetone

k_1 = Rate constant for ketonization

k_2 = Rate constant for enolization

$C = E + K$



$$\frac{-dE}{dt} = k_1 E - k_2 K$$

$$\frac{-dE}{dt} = (k_1 + k_2) E - k_2 C$$

since $A = \epsilon E$

$$\frac{-dA}{dt} = (k_1 + k_2) A - \epsilon k_2 C$$

The slope dA/dt was found by the mirror method and plotted against A . The best straight line was drawn for these points and the slope gave $k_1 + k_2$. The value of ϵ for acetylacetone was calculated from the data in Table VII. For diisobutyrylmethane and dipivaloylmethane ϵ was calculated from the absorbance in the least polar solvent, assuming that these compounds are 100 percent enolized in these solvents as shown by the infrared absorption spectra of the pure liquids. The results are given in Table VII.

Extraction of Alkali Metal Ions with Dipivaloylmethane

Extraction experiments were performed using an ether (reagent grade) solution of dipivaloylmethane, which was shaken with an aqueous solution of the alkali metal ion in

Table VII

Isomerization Rates of beta-Diketones*

Compound	k_1^{**}	k_2^{**}	k_2/k_1
Acetylacetone	917	143	0.156
Diisobutyrylmethane	285	48	0.167
Dipivaloylmethane	47.2	7.8	0.165

*Average values of three runs.

**sec.⁻¹ x 10⁴ ± 10%.

a small glass stoppered addition funnel. After the layers separated, an aliquot of the ether phase was withdrawn and titrated to determine the amount of alkali metal chelate extracted.

The titrations were carried out by either of two methods using a micro buret calibrated to 0.01 ml. in each case. For the non-aqueous titrations an aliquot of the ether layer was mixed with an equal volume of glacial acetic acid and titrated with perchloric acid in dioxane, standardized with potassium acid phthalate dissolved in acetic acid. Methyl violet was used as an indicator but good end-points were not obtained at high chelate concentrations. For the aqueous titrations an aliquote of the

ether layer was shaken with an equal volume of water and the mixture was titrated with standard hydrochloric acid. Thymol blue was used as the indicator with the change from green to yellow being taken as the end-point. The extraction experiments are summarized in Table VIII, and some are shown graphically in Figure 7.

Table VIII

Extraction of Alkali Metal Ions with 0.1N
Dipivaloylmethane in Ether

Initial concentrations in water layer				Vol. ether layer	Vol. water layer	aliquot of ether titrated	0.1N acid titer
K ⁺	Na ⁺	Li ⁺	OH ⁻	ml.	ml.	ml.	
0.5N	-	-	0.5N	25.0	25.0	20	0.07
-	-	0.5	0.5	25.0	25.0	20	14.19
-	0.5	-	0.5	25.0	25.0	20	00.10
-	-	1.0	1.0	25.0	25.0	20	19.82
-	1.0	-	1.0	25.0	25.0	20	0.30
-	2.5	-	2.5	25.0	25.0	20	2.46
-	5.0	-	5.0	25.0	25.0	20	15.83
-	-	0.75	0.75	10.0	10.0	5.0	4.75
-	-	0.25	0.25	10.0	10.0	5.0	1.88
-	-	0.1	0.1	10.0	10.0	5.0	0.46
2.5	-	-	2.5	10.0	10.0	5.0	0.12

Table VIII (continued)

Initial concentrations in water layer				Vol. ether layer	Vol. water layer	Aliquot of ether titrated	0.1N acid titer
K ⁺	Na ⁺	Li ⁺	OH ⁻	ml.	ml.		
1.0	-	-	1.0	10.0	10.0	5.0	0.03
1.0	-	1.0	1.0	10.0	10.0	5.0	4.86
1.0	-	0.5	1.0	10.0	10.0	5.0	4.65
1.0	-	0.2	1.0	10.0	10.0	5.0	3.73
1.0	-	0.05	1.0	10.0	10.0	5.0	1.12
1.0	-	0.025	1.0	10.0	10.0	5.0	0.54
1.0	1.0	-	1.0	10.0	10.0	5.0	0.08
1.0	0.5	-	1.0	10.0	10.0	5.0	0.05
1.0	-	-	1.0	10.0	10.0	5.0	0.02
1.0	2.4	-	1.0	10.0	10.0	5.0	0.14
1.0	-	1.0	1.0	50.0	1.00	25.0	4.48*
1.0	-	1.0	1.0	50.0	1.00	25.0	4.42**
1.0	-	1.0	1.0	50.0	1.00	25.0	4.41
1.0	-	0.5	1.0	50.0	1.00	25.0	2.67

*Concentration of diketone was 0.2N.

**Concentration of diketone was 0.4N.

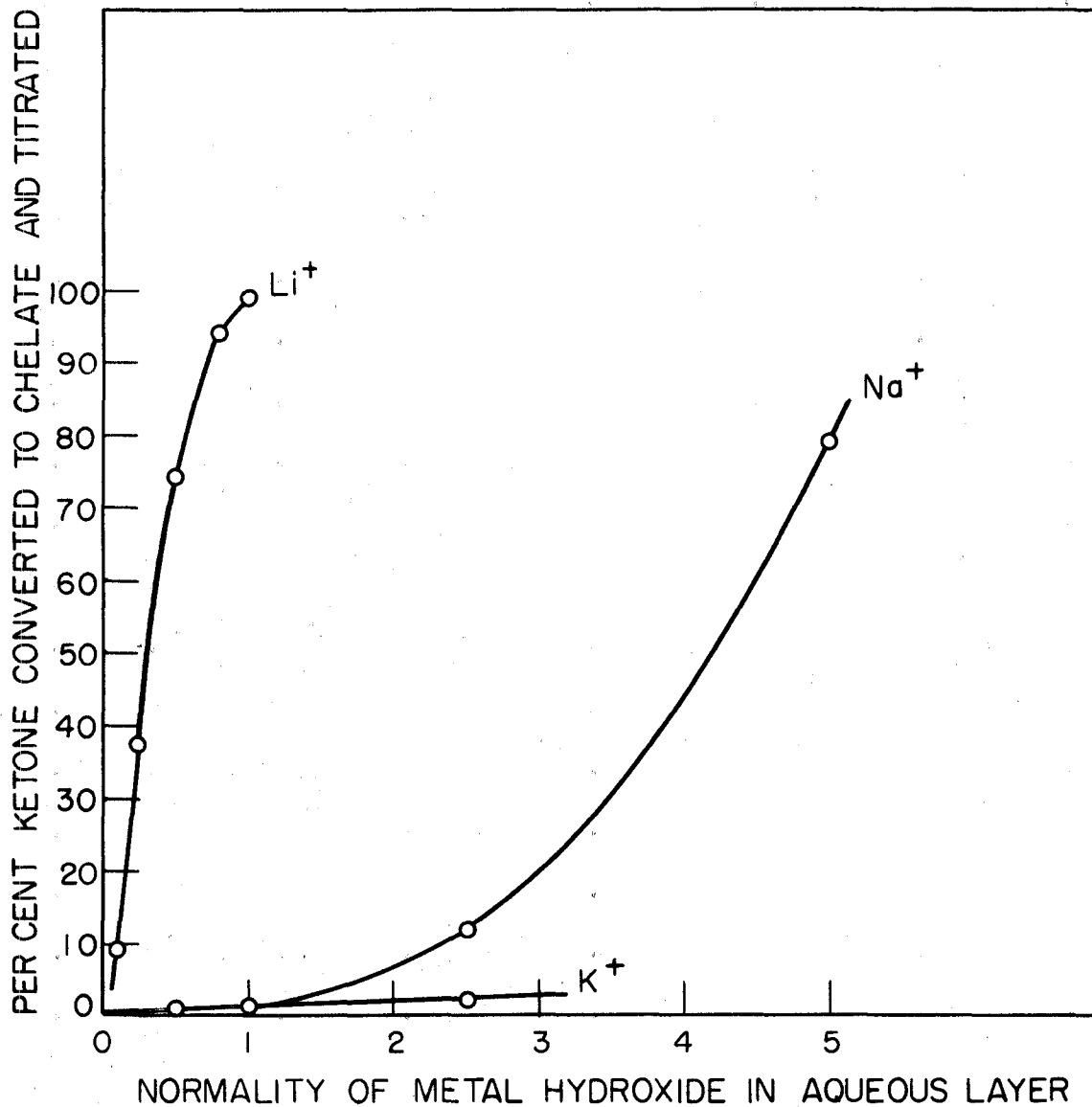


Figure 7

Summary of Extraction Experiments

Equal volumes of the ether and aqueous layers were used
The concentration of DPM was 0.1N.

A suitable procedure for the determination of lithium in the presence of potassium and sodium was found to be as follows: One ml. of a solution 0.500 N in Li^+ , 0.5 N in Na^+ , and 1.0 N in potassium hydroxide in a small separatory funnel for two minutes with 50.0 ml. of 0.1 N dipivaloylmethane in ether. A 25.0 ml. aliquot of the ether solution was mixed with an equal volume of water and titrated with 0.1000 N acid. A total of four such extractions was carried out on four, one ml. samples of the lithium solution; each time as much as possible of the aqueous layer was saved and the four of them were combined. Two ml. of the combined aqueous layers were treated separately with the reagent as above and the aqueous layers again combined. One ml. of the last combined aqueous layers was again treated to obtain a blank titer. The results are given in Table IX.

Table IX

Determination of
0.500 N Solutions of Lithium Ion*

Vol. of 0.0928 N acid required for titer			Calculated $\overline{\text{Li}^+}$
1st extraction	2nd extraction	3rd extraction	
2.859 ml.	0.262	0.239	0.491
2.846	0.265		0.480
2.875			0.491
2.861			0.491

*Prepared using lithium carbonate as the primary standard and dissolving in an equivalent amount of HCl.

Spectrophotometric Measurements of
Acid Dissociation Constants

Method

By measuring the absorbance, A , due to the ionized, K^- , and unionized, KH , species it is possible to calculate an equilibrium constant, K_i , if the extinction coefficients of each species are known.

$$A = \epsilon_{KH} [KH] + \epsilon_{K^-} [K^-]$$

$$C = [K^-] + [KH]$$

$$K_i = \frac{[K^-]}{[KH] [OH^-]}$$

if

$$K_w = [OH^-] [H^+]$$

then

$$K_a = K_e \times K_w$$

For very weak acids the extinction coefficient, ϵ_{KH} , may be measured from the absorbance of a neutral solution. The value for ϵ_{K^-} may only be estimated from a solution of the weak acid highly concentrated in OH^- . The value for K_w in mixed solvents was interpolated from data given by Harned and Owen (36).

Dipivaloylmethane in 50% dioxane.

The absorbance of each solution was read at 294 $m\mu$

where the extinction coefficient for the unionized species was measured as 0.469×10^4 . The total concentration of all species of the diketone was 1.00×10^{-4} molar in each case. The ion product for water in 50 percent dioxane was taken as 2.8×10^{-16} (36) at ionic strength of 0.01 molar. The results of four determinations were the following:

K_1	=	212
K_1	=	212
K_1	=	205
K_1	=	219
<hr/>		
average		212
pKa		= 13.23

Dipivaloylmethane in water

The absorbances were read at $294 \text{ m}\mu$ where the extinction coefficient for the unionized species was measured as 0.113×10^4 and the constant for the anion was estimated 1.93×10^4 . A stock solution of the diketone was prepared in ethanol and diluted one hundred fold with water when used. The ionic strength was held at 0.01 molar with tetramethylammonium bromide. The $\text{[OH}^-]$ used and the results are given in Table X.

Diisobutyrylmethane in water

The absorbances were read at $295 \text{ m}\mu$ where the extinction coefficients for the unionized species was measured as 0.108×10^4 and estimated as 2.03×10^4 for the anion.

The ionic strength was held at 0.01 molar with potassium perchlorate. The results are given in Table XI.

Table X

Determination of pKa of Dipivaloylmethane

$\overline{[\text{OH}^-]} \times 10^4$	$K_1 \times 10^2$	pKa
5.0	1.40	11.85
10	1.73	11.76
15	1.68	11.77
20	1.83	11.74
25	1.84	11.74
50	1.79	11.75
99	1.55	11.81
	average	11.77

Table XI

Determination of pKa of Diisobutyrylmethane

Initial $\overline{[\text{OH}^-]} \times 10^4$	pKa
1.108	10.13
1.662	10.09
2.216	10.05
	average 10.09

Potentiometric Measurement
of Formation Constants

Apparatus

The titrations were carried out in a jacketed beaker having a capacity of about 250 ml. The stopper of the beaker contained nitrogen inlet and outlet, a delivery tube through which the titrant was added, and a stirring apparatus. The micro buret used for measuring out the titrant had a five ml. capacity and could be read to 0.001 ml. Titrations were followed with a Beckman model G pH meter.

Calibration of pH meter

Due to the difficulty in obtaining the true value for hydrogen ion activity from the pH meter in mixed solvents the pH meter was used to read hydrogen ion concentration, and the constants which were obtained are relative concentration constants (37).

The pH meter was standardized against Beckman buffer solution at pH 7.00. One hundred ml. of 75 percent dioxane 0.6925 grams of potassium perchlorate and one ml. of 0.1N perchloric acid placed in the titration vessel and stirred until the potassium perchlorate had dissolved. The mixture was titrated with 0.05N potassium hydroxide in 75 percent dioxane, adding about 0.1 ml. each time.

Making allowance for volume changes the hydrogen ion concentration, $[H^+]$ was calculated and plotted against the reading of the pH meter. A similar plot of $[OH^-]$ against the pH meter readings was made for the basic side of the titration. Both plots were placed on the same graph and adjusted until they both fell on the same straight line. A slope of 1.00 was obtained which indicated a near perfect Nernst slope. It was also found that $[H^+]$ equal pH meter reading plus 0.37. The plot also gave the value for the pK_w of water in this solvent mixture to be 16.87.

Acid dissociation constants of the diketones

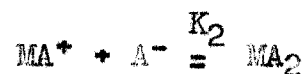
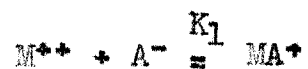
The acid dissociation constants were obtained from the half equivalence points on the potentiometric titration curves. Correction had to be made to the reading obtained for dipivaloylmethane due to its very weak acidic nature and because the dilute solutions used promoted hydrolysis of the anion. The values obtained in 75 percent dioxane 0.05 molar potassium perchlorate are as follows:

Acetylacetone	11.27
Diisobutyrylmethane	12.48
Dipivaloylmethane	14.48

Potentiometric titrations with metal ions and chelating agents

The measurement of formation curves by the potentiometric-

metric method is possible if the following reactions occur.



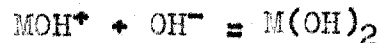
In such a case K_1 and K_2 can be calculated in the usual manner from the formation function.

$$\bar{n} = \frac{K_1 A + 2K_1 K_2 A^2}{1 + K_1 A + K_1 K_2 A^2}$$

A is the molar concentration of the chelating agent with all ionizable protons removed. In the potentiometric method the formation function is easily calculated from $[H^{+}]$ measurements since

$$\bar{n} = \frac{[\text{chelated ligands}]}{[\text{total metal}]} = \frac{[H^{+} \text{ liberated}]}{[\text{total metal}]}$$

If, however, hydrolysis of the monochelate or of the aqueous metal ion occurs as in the following reactions:



it is no longer possible to calculate \bar{n} , since

$$[H^{+} \text{ liberated}] \neq [\text{chelated ligands}]$$

also some of the metal has been removed in the form of the hydrolyzed products. In order to account for the hydrolysis we may still use the potentiometric data and define a new formation function. Brackets are omitted in the following equations:

$$\bar{q} = \frac{\text{bound ligand} + \text{bound OH}^-}{\text{total metal}} = \frac{\text{H}^+ \text{ liberated}}{\text{total metal}}$$

$$\bar{q} = \frac{\text{MA} + 2\text{MA}_2 + 2\text{MAOH} + \text{MOH} + 2\text{M(OH)}_2}{\text{M} + \text{MA} + \text{MA}_2 + \text{MAOH} + \text{MOH} + \text{M(OH)}_2}$$

since

$$K_1 = \frac{\text{MA}}{\text{MA A}}; \quad K_2 = \frac{\text{MA}_2}{\text{MA A}}; \quad K_3 = \frac{\text{MAOH}}{\text{MA OH}}$$

$$K_4 = \frac{\text{MOH}}{\text{M OH}}; \quad K_5 = \frac{\text{M(OH)}_2}{\text{MOH OH}}$$

then

$$\bar{q} = \frac{K_1 A + 2K_1 K_2 A^2 + 2K_1 K_3 A(\text{OH}) + K_4(\text{OH}) + 2K_4 K_5 (\text{OH})^2}{1 + K_1 A + K_1 K_2 A^2 + K_1 K_3 A(\text{OH}) + K_4(\text{OH}) + K_4 K_5 (\text{OH})^2}$$

Although the exact value of \bar{q} may be determined from potentiometric data if pKa of the diketone is large it is not possible to calculate the concentration of A so that a formation curve may be obtained. If, however, a large excess of AH is used so that $\overline{[\text{AH}]}$ remains practically constant A may be calculated. Under these conditions chelation may occur at a low pH where the relative errors

of $\overline{[H^+]}$ measurements are large and \overline{q} can not be accurately measured.

Since it is not possible to solve for the exact value of K_1 and K_2 if hydrolysis occurs, they were obtained assuming that no hydrolysis did occur. Further titrations were then carried out with greater $\overline{[AH]}$. This effectively gave a formation curve at lower pH's or gave less weight to the hydrolysis terms. These values of K_1 and K_2 were then compared with the first values obtained. If they varied outside of experimental error, $\pm .05 \log K$ units, and in a regular manner hydrolysis was considered to be important and formation constants could not be obtained.

Titration procedure

Two to four ml. of the metal ion stock solution of about 0.0125 molar were placed in a titration vessel with 0.6925 grams of potassium perchlorate, five to fifty ml. of 1×10^{-2} molar diketone dissolved in dioxane, and enough water and dioxane to bring the total volume to 100 ml. of 75 percent in dioxane. This mixture was stirred and nitrogen passed through the vessel throughout the titration. After all the potassium perchlorate had dissolved the titration was started, readings being taken at about every 0.10 ml. and as close as possible near the end points.

Formation constants of Zn(II) and Fe(II) chelates

In order to estimate the extent of hydrolysis of the metals in 75 percent dioxane each metal was titrated alone. In most cases precipitation occurred and no definite results could be obtained. Charles and Freiser (38) have shown that the end point obtained corresponded to exactly two equivalents of hydrogen liberated for one mole of bivalent metal ion. When ferrous ion was titrated two end points were obtained indicating the presence of ferric ion or a strong acid impurity. Measurements were therefore not attempted.

Titrations of zinc ion with varying amounts of chelating agents indicated that hydrolysis was important. Although formation curves are tabulated for Zn(II) chelates no values for the formation constants were assigned.

Calculation of formation curves

The formation curves which are tabulated in this section were calculated by the method of Calvin and Wilson (6). The formation constants reported are taken from the formation curves at points where $\bar{n} = 0.5$ and 1.50. In some cases where it was not possible to calculate the formation curve at $\bar{n} = 0.5$ the value for $\log K_1K_2$ was taken from the point where $\bar{n} = 1.00$. The formation curves are given in Tables XII to XLI, and a summary of the formation

constants is given in Table XLII.

Spectrophotometric Estimation of
Formation Constants in 50 Percent Dioxane

Lithium chelate of dipivaloylmethane

The extinction coefficient for the lithium chelate of dipivaloylmethane was taken to be equal to the extinction coefficient of the anion since there was no change in the absorption at the anion peak when lithium perchlorate was added to a solution 1 N in tetramethyl ammonium hydroxide and $1 \times 10^{-4} \text{ N}$ in dipivaloylmethane. Solution of the following equations yielded the values for the calculation of the formation constant.

$$\log \frac{I_0}{I} = \epsilon [\overline{\text{DPM}}] + \epsilon' [\overline{\text{DPM}} + \overline{\text{LiDPM}}]$$

and

$$1 \times 10^{-4} = [\overline{\text{DPM}}] + [\overline{\text{DPM}}] + [\overline{\text{LiDPM}}]$$

The results are summarized in Table XLIII. The concentrations given are the equilibrium concentrations.

Copper chelate of dipivaloylmethane

The ultraviolet absorption spectra of a series of solutions whose concentrations of dipivaloylmethane were held constant and concentration of copper perchlorate varied showed an isobestic point at $288 \text{ m}\mu$. This showed

Table XII
 Formation Curve
 for Acetylacetonone Copper(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.691	3.49	11.62	0.65
1.792	3.55	11.56	0.68
1.902	3.61	11.53	0.75
1.993	3.70	11.44	0.75
2.093	3.80	11.35	0.78
2.196	3.91	11.26	0.84
2.294	4.05	11.14	0.90
2.404	4.24	11.00	1.00
2.495	4.47	10.80	1.08
2.595	4.82	10.51	1.20
2.695	5.20	10.23	1.36
2.795	5.69	9.88	1.54
2.895	6.30	9.54	1.75

*Molar ratio acetylacetonone/Cu(II) = 2.000.

**Concentration 0.0495 molar.

Table XIII

Formation Curve
for Acetylacetonone Copper(II) Chelate*

ml. KOH**	$-\log \overline{[H^+]}$	pA	\bar{n}
2.400	4.02	10.74	.73
2.503	4.21	10.62	1.22
2.598	4.40	10.43	1.26
2.700	4.66	10.18	1.38
2.800	4.97	9.91	1.53
2.912	5.39	9.53	1.72
3.001	5.94	9.01	1.88
3.030	6.36	8.60	1.93
3.080	7.99	6.99	2.03

*Molar ratio acetylacetonone/Cu(II) = 4.000.

**Concentration 0.0495 molar.

Table XIV

Formation Curve
for Acetylacetone Copper(II) Chelate*

ml. KOH**	$-\log [\overline{H^+}]$	pA	\bar{n}
		10.69	1.12
2.291	3.82	10.57	1.14
2.392	3.92	10.48	1.21
2.488	4.06	10.35	1.28
2.592	4.23	10.18	1.36
2.689	4.40	10.02	1.49
2.791	4.63	9.80	1.62
2.897	4.99	9.59	1.77
2.991	5.62	8.83	1.93
3.025	6.16	8.27	2.01

*Molar ratio acetylacetone/Cu(II) = 8.00.

**Concentration 0.0495 molar.

Table XV
 Formation Curve
 for Acetylacetonone Nickel(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
2.200	5.22	9.41	0.05
2.298	5.62	9.04	0.24
2.399	5.97	8.71	0.43
2.505	6.33	8.37	0.58
2.600	6.64	8.09	0.81
2.702	7.07	7.68	1.00
2.800	7.42	7.36	1.18
2.905	7.81	7.00	1.37
3.000	8.18	6.66	1.55
3.099	8.60	6.27	1.72
3.200	9.37	5.54	1.92

*Molar ratio acetylacetonone/Ni(II) = 4.100.

**Concentration .0461 molar.

Table XVI

Formation Curve
for Acetylacetonone Magnesium(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	5.64	8.39	0.00
0.100	6.56	7.47	0.11
0.200	6.94	7.10	0.21
0.300	7.20	6.84	0.31
0.400	7.40	6.65	0.41
0.499	7.57	6.48	0.51
0.600	7.74	6.32	0.62
0.700	7.91	6.15	0.72
0.800	8.07	6.00	0.82
0.900	8.25	5.82	0.92
1.000	8.44	5.64	1.02
1.101	8.62	5.46	1.13
1.200	8.79	5.30	1.22
1.300	8.95	5.14	1.35
1.400	9.08	5.02	1.42
1.500	9.23	4.87	1.51
1.600	9.37	4.74	1.60

*Molar ratio acetylacetonone/Mg(II) = 9.61

**Concentration .0428 N molar.

Table XVI (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.700	9.50	4.62	1.69
1.800	9.62	4.50	1.78
1.899	9.75	4.38	1.86
1.950	9.81	4.32	1.87

Table XVII

Formation Curve
for Acetylacetone Magnesium(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	5.42	8.31	0.00
0.100	6.32	7.41	0.11
0.200	6.68	7.05	0.21
0.300	6.92	6.81	0.31
0.400	7.12	6.62	0.41
0.500	7.29	6.45	0.51
0.600	7.46	6.28	0.62
0.701	7.62	6.12	0.72
0.801	7.78	5.97	0.82

*Molar ratio acetylacetone/Mg(II) = 19.22

**Concentration .0428 molar.

Table XVII (continued)

ml. KOH**	$-\log \sqrt{[H^+]}$	pA	\bar{n}
0.900	7.96	5.79	0.92
1.000	8.12	5.62	1.02
1.100	8.31	5.44	1.12
1.200	8.48	5.28	1.22
1.299	8.63	5.13	1.34
1.400	8.77	4.99	1.42
1.500	8.92	4.84	1.51
1.599	9.04	4.73	1.60
1.700	9.17	4.60	1.69
1.800	7.30	4.47	1.77
1.900	9.40	4.37	1.85
2.000	9.53	4.25	1.92

Table XVIII

Formation Curve
for Acetylacetonate Cobalt(II) Chelate*

ml. KOH**	$-\log \sqrt{[H^+]}$	pA	\bar{n}
0.000	4.77	9.56	0.00
0.097	5.17	9.17	0.09

*Molar ratio acetylacetonate/Co(II) = 4.171.

**Concentration .0428 molar.

Table XVIII (continued)

ml. KOH**	$-\log \bar{M}_w$	pA	\bar{n}
0.197	5.47	8.88	0.18
0.297	5.70	8.66	0.26
0.396	5.88	8.49	0.35
0.497	6.07	8.31	0.44
0.598	6.22	8.17	0.53
0.698	6.37	8.03	0.62
0.798	6.51	7.90	0.71
0.899	6.67	7.75	0.80
0.999	6.82	7.61	0.89
1.097	7.00	7.44	0.98
1.198	7.18	7.28	1.07
1.298	7.35	7.12	1.16
1.398	7.51	6.97	1.25
1.499	7.68	6.82	1.34
1.598	7.83	6.68	1.42
1.699	7.98	6.55	1.51
1.798	8.17	6.37	1.60
1.903	8.38	6.18	1.70
1.999	8.61	5.96	1.78
2.098	8.91	5.68	1.87
2.199	9.40	5.12	1.95

Table XIX

Formation Curve
for Acetylacetone Manganese(II) Chelate*

ml. KOH**	$-\log [\overline{H^+}]$	pA	\bar{n}
0.000	5.16	8.87	0.00
0.099	5.85	8.18	0.09
0.199	6.20	7.84	0.18
0.298	6.44	7.60	0.27
0.399	6.62	7.43	0.36
0.499	6.78	7.27	0.45
0.599	6.93	7.13	0.53
0.699	7.07	6.99	0.62
0.799	7.21	6.86	0.71
0.901	7.35	6.72	0.80
1.000	7.49	6.59	0.89
1.099	7.63	6.45	0.98
1.200	7.79	6.30	1.07
1.299	7.94	6.15	1.17
1.398	8.09	6.01	1.24
1.499	8.25	5.85	1.33
1.599	8.38	5.73	1.42

*Molar ratio acetylacetone/Mn(II) = 8.30.

**Concentration .0428 molar.

Table XIX (continued)

ml. KOH**	$-\log \frac{[\bar{H}^+]}{[H^+]}$	pA	\bar{n}
1.699	8.52	5.60	1.50
1.800	8.66	5.46	1.59
1.899	8.79	5.34	1.68
1.999	8.95	5.18	1.76
2.099	9.09	5.05	1.85
2.199	9.26	4.89	1.93

Table XX

Formation Curve
for Acetylacetone Manganese(II) Chelate*

ml. KOH**	$-\log \frac{[\bar{H}^+]}{[H^+]}$	pA	\bar{n}
0.000	5.03	8.70	0.00
0.100	5.64	8.09	0.09
0.200	5.97	7.76	0.18
0.300	6.19	7.54	0.27
0.400	6.37	7.37	0.36
0.500	6.53	7.21	0.45
0.600	6.67	7.07	0.53

*Molar ratio acetylacetone/Mn(II) = 16.60.

**Concentration .0428 molar.

Table XX (continued)

ml. KOH***	$-\log [\bar{H}^+]$	pA	\bar{n}
0.703	6.79	6.95	0.63
0.799	6.92	6.83	0.71
0.901	7.08	6.67	0.80
1.000	7.24	6.51	0.89
1.100	7.40	6.35	0.98
1.201	7.56	6.20	1.07
1.300	7.71	6.05	1.17
1.399	7.87	5.89	1.24
1.501	8.01	5.75	1.33
1.600	8.16	5.61	1.42
1.700	8.29	5.48	1.50
1.800	8.45	5.32	1.59
1.900	8.59	5.18	1.67
2.000	8.75	5.03	1.75
2.100	8.93	4.85	1.84
2.201	9.14	4.64	1.91

Table XXI

Formation Curve
for Acetylacetonone Zinc(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	4.31	9.02	0.00
0.101	4.52	8.81	0.88
0.200	4.73	8.60	0.17
0.300	4.89	8.44	0.25
0.401	5.04	8.29	0.34
0.500	5.19	8.14	0.42
0.600	5.31	8.02	0.51
0.699	5.43	7.90	0.59
0.798	5.54	7.79	0.68
0.898	5.67	7.66	0.76
1.001	5.79	7.54	0.84
1.100	5.91	7.42	0.93
1.200	6.03	7.30	1.01
1.300	6.14	7.19	1.11
1.400	6.26	7.08	1.18
1.498	6.37	6.97	1.27
1.600	6.49	6.85	1.35

*Molar ratio acetylacetonone/Zn(II) = 39.87.

**Concentration .0428 molar.

Table XXI (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.701	6.60	6.74	1.43
1.800	6.73	6.61	1.52
1.900	6.87	6.47	1.60
2.000	7.03	6.31	1.69
2.100	7.25	6.09	1.77
2.200	7.53	5.81	1.86

Table XXII

Formation Curve
for Dipivaloylmethane Copper(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.394	3.29	13.79	.67
1.601	3.39	13.68	.62
2.200	3.79	13.30	.78
2.800	5.08	12.03	1.29
2.980	5.38	11.75	1.46
3.000	5.78	11.36	1.64

*Molar ratio dipivaloylmethane/Cu(II) = 12.00.

**Concentration .0469 molar.

Table XXIII

Formation Curve
for Dipivaloylmethane Copper(II) Chelate*

ml. KOH**	$-\log [\overline{H^+}]$	pA	\bar{n}
1.795	3.59	13.99	.40
1.995	3.74	13.85	.48
2.100	3.84	13.76	.52
2.193	3.94	13.67	.58
2.295	4.07	13.54	.65
2.393	4.23	13.40	.73
2.495	4.48	13.18	.82
2.606	4.91	12.74	.93
2.695	5.27	12.40	1.08
2.795	5.63	12.07	1.25
2.895	5.98	11.75	1.44
2.996	6.37	11.39	1.62
3.096			1.80
3.196			2.00

*Molar ratio dipivaloylmethane/Cu(II) = 4.000.

**Concentration .0469 molar.

Table XXIV

Formation Curve
for Dipivaloylmethane Copper(II) Chelate*

ml. KOH**	$-\log [\overline{H^+}]$	pA	\bar{n}
1.192	3.25	14.01	.48
1.395	3.33	13.93	.49
1.595	3.43	13.83	.48
1.797	3.54	13.72	.527
1.995	3.67	13.60	.600
2.105	3.77	13.50	.630
2.197	3.85	13.42	.68
2.295	3.98	13.30	.72
2.393	4.14	13.14	.78
2.497	4.37	12.92	.85
2.595	4.67	12.62	.964
2.698	5.03	12.27	1.10
2.795	5.34	11.97	1.25
2.897	5.68	11.64	1.44
2.995	6.10	11.24	1.63
3.097			1.81
3.198			2.00

*Molar ratio dipivaloylmethane/Cu(II) = 8.00.

**Concentration .0469 molar.

Table XXV

Formation Curve
for Dipivaloylmethane Magnesium(II) Complex*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	6.91	10.02	0.000
0.104	8.54	8.39	0.1072
0.200	8.96	7.98	0.206
0.300	9.17	7.77	0.310
0.400	9.32	7.63	0.410
0.500	9.46	7.49	0.515
0.601	9.58	7.38	0.618
0.701	9.68	7.28	0.722
0.800	9.77	7.20	0.825
0.900	9.87	7.10	0.929
0.999	9.94	7.04	1.030
1.100	10.03	6.95	1.132
1.200	10.11	6.88	1.237
1.300	10.20	6.79	1.361
1.400	10.29	6.71	1.442
1.500	10.39	6.61	1.546
1.600	10.51	6.50	1.648

*Molar ratio dipivaloylmethane/Mg(II) = 9.61.

**Concentration .0428 molar.

Table XXV (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.700	10.66	6.35	1.750
1.800	10.86	6.16	1.85
1.900	11.12	5.90	1.95

Table XXVI

Formation Curve
for Dipivaloylmethane Magnesium(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	7.00	9.63	0.000
0.103	8.38	8.25	0.107
0.200	8.70	7.93	0.21
0.300	8.91	7.72	0.31
0.401	9.07	7.57	0.41
0.500	9.17	7.47	0.52
0.600	9.27	7.37	0.62
0.700	9.37	7.27	0.72
0.800	9.47	7.18	0.83
0.900	9.57	7.08	0.93

*Molar ratio dipivaloylmethane/Mg(II) = 19.22.

**Concentration .0428 molar.

Table XXVI (continued)

ml. KOH***	$-\log [\bar{H}^+]$	pA	\bar{n}
1.000	9.63	7.02	1.03
1.101	9.74	6.91	1.13
1.200	9.82	6.84	1.23
1.300	9.90	6.76	1.36
1.401	9.99	6.67	1.44
1.500	10.08	6.58	1.55
1.600	10.21	6.46	1.65
1.700	10.36	6.31	1.75
1.801	10.56	6.11	1.85
1.901	10.86	5.81	1.96
1.925	11.02	5.65	1.99

Table XXVII

Formation Curve
for Dipivaloylmethane Cobalt(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	5.56	11.37	0.00
0.102	6.50	10.43	0.10

*Molar ratio dipivaloylmethane/Co(II) = 18.00.

**Concentration .0428 molar.

Table XXVII (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.201	6.82	10.12	0.19
0.300	7.04	9.90	0.29
0.400	7.17	9.78	0.38
0.500	7.28	9.67	0.48
0.600	7.41	9.55	0.58
0.700	7.50	9.46	0.67
0.801	7.59	9.38	0.77
0.899	7.67	9.30	0.88
1.001	7.74	9.27	0.96
1.100	7.82	9.16	1.06
1.200	7.90	9.09	1.16
1.300	7.98	9.01	1.27
1.400	8.06	8.94	1.35
1.500	8.15	8.85	1.44
1.600	8.23	8.78	1.54
1.700	8.31	8.71	1.64
1.800	8.43	8.59	1.73
1.901	8.55	8.48	1.83
2.000	8.88	8.15	1.92

Table XXVIII

Formation Curve
for Dipivaloylmethane Cobalt(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	5.56	11.37	0.00
0.102	6.50	10.43	0.10
0.201	6.82	10.12	0.19
0.300	7.04	9.90	0.29
0.400	7.17	9.78	0.38
0.500	7.28	9.67	0.48
0.600	7.41	9.55	0.58
0.700	7.50	9.46	0.67
0.801	7.59	9.38	0.77
0.899	7.67	9.30	0.87
1.001	7.74	9.24	0.96
1.100	7.82	9.16	1.06
1.200	7.90	9.09	1.16
1.300	7.98	9.01	1.27
1.400	8.06	8.94	1.35
1.500	8.15	8.85	1.44
1.600	8.23	8.78	1.54

*Molar ratio dipivaloylmethane/Co(II) = 8.99.

**Concentration .0428 molar.

Table XXVIII (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.700	8.31	8.71	1.67
1.800	8.43	8.59	1.73
1.901	8.55	8.48	1.83
2.000	8.88	8.15	1.92

Table XXIX

Formation Curve
for Dipivaloylmethane Cobalt(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	5.39	11.24	0.00
0.104	6.21	10.42	0.09
0.198	6.53	10.10	0.18
0.299	6.69	9.94	0.27
0.400	6.83	9.81	0.36
0.500	6.93	9.71	0.45
0.600	7.03	9.61	0.54
0.700	7.14	9.50	0.63
0.799	7.21	9.44	0.71

*Molar ratio dipivaloylmethane/Co(II) = 16.66.

**Concentration .0428 molar.

Table XXIX (continued)

ml. KOH***	$-\log [\bar{H}^+]$	pA	\bar{n}
0.900	7.28	9.37	0.80
0.999	7.34	9.31	0.89
1.100	7.42	9.23	0.98
1.200	7.49	9.17	1.07
1.301	7.57	9.09	1.18
1.400	7.64	9.02	1.25
1.501	7.70	8.96	1.34
1.600	7.80	8.87	1.43
1.700	7.88	8.79	1.52
1.800	7.95	8.72	1.61
1.900	8.03	8.64	1.70
1.999	8.15	8.53	1.78
2.100	8.42	8.26	1.88
2.200	9.76	6.92	1.96

Table XXX

Formation Curve
for Dipivaloylmethane Nickel(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
2.191	6.69	10.84	0.04
2.289	7.30	10.25	0.22
2.391	7.58	10.00	0.41
2.492	7.80	9.80	0.61
2.588	7.94	9.68	0.79
2.691	8.06	9.59	0.98
2.791	8.19	9.49	1.17
2.891	8.35	9.35	1.36
2.991	8.52	9.22	1.55
3.090	8.78	8.99	1.74
3.190	9.21	8.60	1.92

*Molar ratio dipivaloylmethane/Ni(II) = 4.100.

**Concentration .0461 molar.

Table XXXI

Formation Curve
for Dipivaloylmethane Nickel(II) Chelate*

ml. KOH**	$-\log [H^+]$	pA	\bar{n}
2.195	6.35	10.58	0.04
2.293	6.77	10.16	0.23
2.392	6.97	9.97	0.41
2.495	7.14	9.80	0.61
2.591	7.26	9.69	0.79
2.696	7.40	9.55	0.99
2.793	7.53	9.43	1.18
2.895	7.67	9.30	1.36
2.993	7.94	9.03	1.55
3.094	8.13	8.85	1.74
3.197	8.74	8.24	1.93

*Molar ratio dipivaloylmethane/Ni(II) = 16.40.

**Concentration .0461 molar.

Table XXXII

Formation Curve
for Dipivaloylmethane Nickel(II) Chelate*

ml. KOH**	$-\log [\overline{H^+}]$	pA	\bar{n}
2.200	6.05	10.48	0.05
2.300	6.41	10.12	0.24
2.398	6.60	9.93	0.43
2.452	6.68	9.85	0.52
2.512	6.76	9.78	0.64
2.551	6.81	9.73	0.71
2.601	6.86	9.68	0.81
2.650	6.93	9.61	0.90
2.704	7.01	9.53	1.00
2.750	7.07	9.47	1.09
2.798	7.13	9.41	1.18
2.850	7.22	9.32	1.28
2.898	7.31	9.24	1.37
2.953	7.40	9.15	1.48
2.998	7.49	9.06	1.56
3.051	7.61	8.94	1.66
3.102	7.79	8.76	1.75

*Molar ratio dipivaloylmethane/Ni(II) = 41.00.

Table XXXII (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
3.152	8.06	8.49	1.84
3.196	8.48	8.07	1.93
3.249	11.00	5.00	2.01

Table XXXIII

Formation Curve
for Dipivaloylmethane Manganese(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	6.43	10.20	0.00
0.100	7.13	9.50	0.09
0.201	7.58	9.05	0.18
0.300	7.84	8.79	0.27
0.400	8.02	8.62	0.36
0.500	8.16	8.48	0.45
0.601	8.29	8.35	0.53
0.700	8.38	8.26	0.63
0.800	8.47	8.18	0.71
0.901	8.55	8.10	0.80

*Molar ratio dipivaloylmethane/Mn(II) = 16.60.

**Concentration .0428 molar.

Table XXXIII (continued)

ml. KOH***	$-\log [\text{H}^+]$	pA	\bar{n}
1.000	8.63	8.02	0.89
1.100	8.71	7.94	0.98
1.200	8.79	7.87	1.07
1.300	8.86	7.80	1.17
1.408	8.94	7.72	1.24
1.500	9.03	7.63	1.33
1.600	9.11	7.56	1.42
1.700	9.20	7.47	1.51
1.800	9.32	7.38	1.60
1.900	9.46	7.21	1.69
2.006	9.64	7.04	1.78
2.100	9.90	6.78	1.87
2.200	10.50	6.18	1.96

Table XXXIV

Formation Curve
for Dipivaloylmethane Manganese(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	6.16	10.77	0.00
0.100	7.33	9.60	0.09
0.200	7.86	9.08	1.18
0.300	8.18	8.76	0.27
0.401	8.36	8.59	0.36
0.500	8.50	8.45	0.45
0.600	8.61	8.35	0.53
0.700	8.71	8.25	0.63
0.800	8.80	8.17	0.71
0.900	8.88	8.09	0.80
1.000	8.95	8.03	0.89
1.100	9.03	7.95	0.98
1.200	9.10	7.89	1.07
1.300	9.18	7.81	1.17
1.400	9.26	7.74	1.24
1.500	9.34	7.66	1.33
1.600	9.42	7.59	1.42
1.700	9.51	7.51	1.51

*Molar ratio dipivaloylmethane/Mn(II) = 8.32.

**Concentration .0428 molar.

Table XXXIV (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.800	9.63	7.39	1.60
1.901	9.76	7.27	1.69
2.000	9.90	7.13	1.78
2.100	10.12	6.92	1.87
2.201	10.53	6.52	1.96

Table XXXV

Formation Curve
for Dipivaloylmethane Zinc(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	4.17	11.88	0.00
0.101	5.62	10.41	0.88
0.200	5.86	10.17	0.17
0.301	6.05	9.98	0.25
0.400	6.18	9.85	0.34
0.499	6.30	9.73	0.42
0.600	6.39	9.64	0.51
0.700	6.49	9.54	0.59
0.799	6.56	9.47	0.68

*Molar ratio dipivaloylmethane/Zn(II) = 15.76.

**Concentration .0428 molar.

Table XXXV (continued)

ml. KOH***	$-\log \overline{[H^+]}$	pA	\bar{n}
0.900	6.64	9.39	0.76
1.000	6.70	9.33	0.84
1.101	6.77	9.26	0.93
1.200	6.84	9.19	1.01
1.300	6.92	9.11	1.11
1.399	6.98	9.05	1.18
1.500	7.06	8.97	1.27
1.600	7.14	8.89	1.35
1.700	7.22	8.82	1.43
1.800	7.32	8.72	1.52
1.900	7.41	8.63	1.60
2.000	7.53	8.51	1.69
2.100	7.68	8.36	1.77
2.200	7.93	8.11	1.86
2.300	8.36	7.68	1.950

Table XXXVI

Formation Curve
for Dipivaloylmethane Zinc(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	5.14	11.19	0.00
0.100	5.79	10.54	0.88
0.200	6.17	10.16	0.17
0.300	6.33	10.00	0.25
0.400	6.46	9.87	0.34
0.500	6.59	9.74	0.42
0.600	6.68	9.65	0.51
0.702	6.77	9.56	0.59
0.800	6.85	9.48	0.68
0.900	6.93	9.41	0.76
1.000	7.00	9.34	0.84
1.101	7.09	9.25	0.93
1.201	7.16	9.18	1.01
1.300	7.22	9.12	1.11
1.401	7.29	9.05	1.18
1.500	7.37	8.97	1.27
1.600	7.44	8.90	1.35
1.700	7.53	8.82	1.43

*Molar ratio dipivaloylmethane/Zn(II) = 31.52.

**Concentration .0428 molar.

Table XXXVI (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.800	7.62	8.73	1.52
1.900	7.73	8.62	1.60
2.002	7.86	8.49	1.69
2.101	7.99	8.36	1.77
2.200	8.20	8.15	1.86
2.309	8.56	5.78	1.95

Table XXXVII

Formation Curve
for Diisobutyrylmethane Copper(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	3.45	11.61	0.724
0.100	3.51	11.55	0.744
0.200	3.56	11.50	0.789
0.309	3.62	11.45	0.826
0.400	3.68	11.39	0.878
0.500	3.75	11.33	0.929
0.600	3.86	11.22	0.962

*Molar ratio diisobutyrylmethane/Cu(II) = 4.078.

**Concentration .0556 molar.

Table XXXVII (continued)

ml. KOH***	$-\log [\text{H}^+]$	pA	\bar{n}
0.700	3.97	11.11	1.010
0.800	4.14	10.95	1.053
0.901	4.32	10.77	1.116
1.000	4.52	10.57	1.192
1.100	4.73	10.37	1.280
1.200	4.93	10.18	1.385
1.300	5.11	10.01	1.489
1.400	5.33	9.80	1.595
1.500	5.56	9.59	1.705
1.551	5.72	9.43	1.761
1.600	5.86	9.30	1.812
1.650	6.05	9.11	1.868
1.700	6.31	8.86	1.925
1.725	6.60	8.57	1.953
1.750	7.13	8.04	1.982

Table XXVIII

Formation Curve
for Diisobutyrylmethane Nickel(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	4.90	9.98	0.000
0.100	5.43	9.45	0.109
0.200	5.84	9.05	0.228
0.299	5.95	8.95	0.341
0.399	6.13	8.77	0.455
0.500	6.26	8.65	0.569
0.600	6.41	8.51	0.686
0.700	6.53	8.38	0.796
0.800	6.65	8.28	0.909
0.900	6.77	8.17	1.023
0.999	6.92	8.02	1.138
1.099	7.07	7.88	1.250
1.202	7.23	7.73	1.368
1.300	7.37	7.59	1.480
1.400	7.57	7.40	1.592
1.500	7.82	7.16	1.707

*Molar ratio diisobutyrylmethane/Ni(II) = 8.18.

**Concentration .0556 molar.

Table XXXVIII (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.600	8.09	6.90	1.820
1.700	8.77	6.23	1.932
1.800	10.69	4.31	2.05

Table XXXIX

Formation Curve
for Diisobutyrylmethane Magnesium(II) Chelate*

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.000	6.27	8.61	0.000
0.101	7.59	7.29	0.134
0.200	8.03	6.86	0.267
0.299	8.30	6.60	0.400
0.398	8.50	6.40	0.534
0.500	8.67	6.24	0.669
0.600	8.81	6.11	0.800
0.698	8.95	5.97	0.933
0.800	9.08	5.85	1.066
0.900	9.22	5.72	1.198

*Molar ratio diisobutyrylmethane/Mg(II) = 10.42.

**Concentration .0556 molar.

Table XXXIX (continued)

ml. KOH***	$-\log [\text{H}^+]$	pA	\bar{n}
0.999	9.34	5.60	1.330
1.100	9.47	5.48	1.460
1.200	9.61	5.35	1.593
1.300	9.75	5.21	1.723
1.400	9.91	5.06	1.848
1.500	10.07	4.91	1.972
1.600	10.24	4.75	2.091

Table XL

Formation Curve
for Diisobutyrylmethane Cobalt(II) Chelate*

ml. KOH**	$-\log [\text{H}^+]$	pA	\bar{n}
0.000	5.05	9.83	0.000
0.101	5.74	9.14	0.107
0.200	6.06	8.83	0.214
0.300	6.29	8.61	0.320
0.400	6.46	8.44	0.427
0.500	6.61	8.30	0.535

*Molar ratio diisobutyrylmethane/Mn(II) = 7.69.

**Concentration .0556 molar.

Table XL (continued)

ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
0.600	6.73	8.19	0.644
0.701	6.84	8.08	0.748
0.801	6.96	7.97	0.855
0.900	7.07	7.87	0.962
1.003	7.19	7.75	1.069
1.100	7.28	7.67	1.174
1.200	7.39	7.57	1.285
1.302	7.53	7.43	1.390
1.400	7.67	7.30	1.497
1.500	7.83	7.15	1.604
1.600	8.00	6.99	1.710
1.700	8.28	6.72	1.820
1.800	8.81	6.19	1.923

Table XLI

Formation Curve
for Diisobutyrylmethane Manganese(II) Chelate*

ml. KOH**	$-\log [\text{H}^+]$	pA	\bar{n}
0.000	5.74	9.14	0.000
0.100	6.75	8.13	0.107
0.202	7.14	7.75	0.214
0.300	7.37	7.53	0.321
0.400	7.59	7.31	0.428
0.501	7.73	7.18	0.536
0.600	7.86	7.06	0.643
0.700	8.00	6.92	0.749
0.801	8.13	6.80	0.856
0.900	8.25	6.69	0.964
1.000	8.36	6.58	1.070
1.100	8.50	6.45	1.175
1.200	8.62	6.34	1.287
1.300	8.75	6.21	1.392
1.400	8.89	6.08	1.498
1.500	9.04	5.94	1.607

*Molar ratio diisobutyrylmethane/Mn(II) = 7.71.

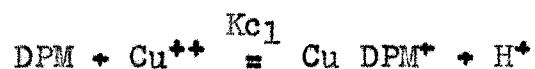
**Concentration .0556 molar.

Table XLI (continued)

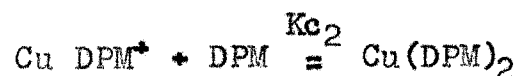
ml. KOH**	$-\log [\bar{H}^+]$	pA	\bar{n}
1.600	9.24	5.75	1.712
1.700	9.47	5.53	1.820
1.800	9.88	5.12	1.928

the presence of only two species absorbing in this region. The absorption band peaking at 300 $m\mu$ was taken as that due to some chelated form of dipivaloylmethane. The method of continuous variations was used to indicate the formula of the chelate. The method revealed a mixture of 1-1 and 2-1 chelate. Therefore, the extinction coefficient of bound chelate was assumed to be the same whether it is in the form of a 1-1 or 2-1 chelate.

From the absorbance at 300 $m\mu$ the constant for the reaction



and



could be calculated. This was possible since the absorbance at 300 $m\mu$ could be used to calculate $[\bar{DPM}]$ and $[\bar{\text{bound DPM}}]$ assuming that in a neutral solution $[\bar{DPM}]$ was negligible

Table XLII

Formation Constants of beta-Diketones

Acetylacetone				Diisobutyrylmethane		
Metal	$\log K_1$	$\log K_2$	$\log K_1/K_2$	$\log K_1$	$\log K_2$	$\log K_1/K_2$
Cu(II)	11.57	9.64	1.90	12.29	9.99	2.30
Ni(II)	8.24	6.39	1.25	8.73	7.56	1.17
Co(II)	7.86	6.19	1.67	8.37	7.31	1.01
Mn(II)	6.81	5.18	1.63	7.23	6.07	1.16
Mg(II)	6.13	4.52	1.61	6.45	5.44	1.01

Dipivaloylmethane			
Metal	$\log K_1$	$\log K_2$	$\log K_1/K_2$
Cu(II)	13.91	11.55	2.36
Ni(II)	9.90	9.10	0.80
Co(II)	9.60	8.77	0.83
Mn(II)	8.34	7.44	0.90
Mg(II)	7.44	6.59	0.85

and using the equations

$$[\overline{\text{DPM}}] + [\overline{\text{bound DPM}}] = 1 \times 10^{-4}$$

$$\log \frac{I_0}{I} = \epsilon [\overline{\text{DPM}}] + \epsilon_1 [\overline{\text{bound DPM}}]$$

ϵ_1 was taken from a solution saturated with $\text{Cu}(\text{NO}_3)_2$ and containing 1×10^{-4} N dipivaloylmethane. Knowing the total bound chelate the points could be placed on a Bjerrum formation curve, or \bar{n} was determined from

$$\bar{n} = \frac{[\overline{\text{bound ligand}}]}{[\overline{\text{total metal}}]}$$

From two points on the formation curve an estimation of K_1 was made where \bar{n} equals 0.5 and K_2 was calculated, from the values on the formation curve where \bar{n} equals 1.50. Using this value for K_2 a new value of K_1 was calculated from the values given where \bar{n} equals 0.5. This process was repeated until agreement was obtained. The formation function used in each case was

$$\bar{n} = \frac{K_1 [\overline{\text{DPM}}] [\overline{\text{H}^+}] + 2 K_1 K_2 [\overline{\text{DPM}}]^2}{[\overline{\text{H}^+}]^2 + K_1 [\overline{\text{DPM}}] [\overline{\text{H}^+}] + K_1 K_2 [\overline{\text{DPM}}]^2}$$

where $[\overline{\text{DPM}}]$ is the molar concentration of the unionized species. The $[\overline{\text{H}^+}]$ was taken to be equal to the bound ligand concentration. The two values obtained for K_1 and K_2 are:

$$\log K_1 = 13.40$$

$$\log K_2 = 12.78$$

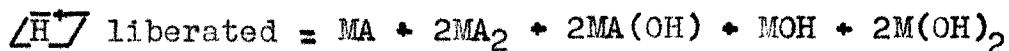
where

$$K_n = \frac{Kc_n}{K_1 K_w} \quad K_1 = \frac{[\overline{\text{DPM}}]}{[\overline{\text{DPM}}] [\overline{\text{OH}}]}$$

$$\text{and } K_w = 2.8 \times 10^{-16} \quad (36)$$

Since potentiometric titrations of copper metal ion in 50 percent dioxane (38) showed that considerable hydrolysis of the metal takes place at low pH readings, the formation constants determined by this method do not agree at all with the potentiometric method. It is probable also that some hydrolysis of the monochelated metal occurs and that the absorption characteristics are similar to those of MA and MA₂.

In this case suitable concentration ranges were not used so that formation and hydrolysis constants could not be obtained by the use of the two methods simultaneously. A method employing both techniques would be useful in this regard since the potentiometric method enables the measurement of $[\overline{\text{H}}^+]$ liberated.



Spectrophotometric measurement would give $[\overline{\text{bound chelate}}]$.



then if we ignore MOH and $\text{M}(\text{OH})_2$



An estimation of the amount of metal in the form of MOH and $\text{M}(\text{OH})_2$ may be made from the potentiometric titration curve of the metal ion alone. Difficulty was encountered in attempts to make this measurement when precipitation occurred early in the titration when 75 percent dioxane was used.

Table XLIII

Determination of Formation Constant of the Lithium
Chelate of Dipivaloylmethane in 50 Percent Water-Dioxane

Concentrations of substituents			log K_1
$\text{OH}^- \times 10^4$	$\text{Li}^+ \times 10^4$	$\text{DPM}^- \times 10^4$	
.0106	2.19	.477	3.47
.0106	2.19	.477	3.47
.0106	4.51	.355	3.48

DISCUSSION

Infrared and Ultraviolet Spectra

The close similarity of the infrared spectra of dipivaloylmethane and its lithium chelate clearly indicate the similarity of their structures. It is, however, difficult to account for a weak and diffuse band occurring in the chelating agent at about 2600 wave numbers unless this is assigned to the OH stretching frequency. This assignment was made when this band did not appear in the copper chelate and shifted to longer wavelengths for the deuterated chelating agent. This assignment was also made by Rasmussen (39). The spectra obtained at high resolution using lithium fluoride optics did not reveal any simple relationship to the fact that the enol form of beta-diketones contains an aromatic hydrogen.

The enolic content of beta-diketones can be revealed by their infrared spectra. K. Kuratani (35) has developed an analytical method for enol content based upon the absorption of the carbonyl and conjugated carbonyl groups at 1710 and 1600 cm.^{-1} respectively. Kuratani found that *p*-methoxybenzoylpivaloylmethane was 100 percent enolized in non polar solvents by this method. Spectra of diisobutyrylmethane and dipivaloylmethane reveal no unconjugated

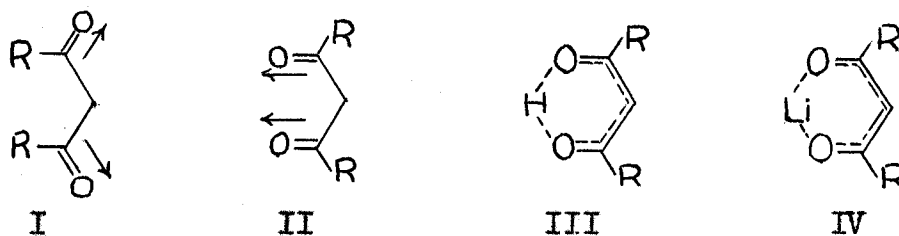
carbonyl (diketone form) in the pure liquid. Further evidence can be obtained from the ultraviolet spectra where the extinction coefficient remains high for dipivaloylmethane in acetonitrile and decreases in the series toward acetylacetone. Water appears to exert a leveling effect upon the keto-enol equilibrium since all are 15 to 18 percent enolized in this solvent.

It has been shown that the introduction of alkyl groups on the methylene groups of acetylacetone and acetoacetic esters decreases the tendency to enolize (40). This is explained by the steric hindrance between the methyl groups of the cyclic enol form. The infrared absorption spectra of 3-methylacetylacetone reveals a strong OH stretching frequency undoubtedly due to the enol being largely present in the acyclic form. Considerable absorption is also noted at 1710 cm.^{-1} indicating a large amount of the diketone form.

Examination of molecular models reveals how increasing the steric requirements on the terminal methyl groups of acetylacetone may increase the enol content. It is possible to construct models corresponding to structure I and II for acetylacetone.

Dipivaloylmethane and diisobutyrylmethane may be constructed only in the form II in which the steric hindrance

between the R groups is minimum and the repulsion between the carbonyl dipoles is maximum. Such a structure as II is stabilized when a proton is removed from the methylene carbon and placed between the two carbonyl dipoles to form the enol III. Thus, the stability of the diketone form is reduced as the steric requirements of the R groups increase.



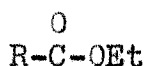
Evidence to indicate that Structure III is that of the enol form is the largely displaced carbonyl stretching frequency appearing at 1600 cm.^{-1} which differs greatly from the normal carbonyl stretching frequency (above 1700 cm.^{-1}). The similarity of the absorption spectra of the chelating agent and that of the lithium chelate especially in the 1600 cm.^{-1} region also supports Structure III. The chelate is shown in Structure IV.

Variation of Acidity with Steric Requirements

The same factors which were used above to describe the instability of the diketone form where R is large may be used to describe the instability of the anions of the same compounds. Here the dipolar repulsion of the carbonyl

groups is augmented in the absence of the shielding proton and with a full negative charge concentrated on the carbonyls.

A striking correlation is found between the rates of alkaline hydrolysis of ethyl esters in 85 percent ethanol of the compounds



and the pKa of the beta-diketones where the R group of the ester is the same as the terminal R groups of the beta-diketones. The same correlation exists for the rate constants of ketonization (or enolization). The excellent linear relationship is shown in Figure 8. The agreement is so good that fortuity does not give a satisfactory explanation. Hammett has demonstrated that such linearity commonly exists only for meta and para substituted benzoic acid derivatives (41). In the case of the ester hydrolysis of aliphatic esters $\Delta\Delta s^\ddagger$ does not remain constant as the series where R equals methyl, i-propyl, and t-butyl progresses. That $\Delta\Delta s^\ddagger$ remains zero or nearly so for a series of meta and para substituted benzoic acid derivatives is demonstrated by Hammett and helps constitute a simple explanation for the correlation of structure and reactivity. It is not understood why linearity should appear in this case. Enolization requires an attack by a base on the methylene carbon,

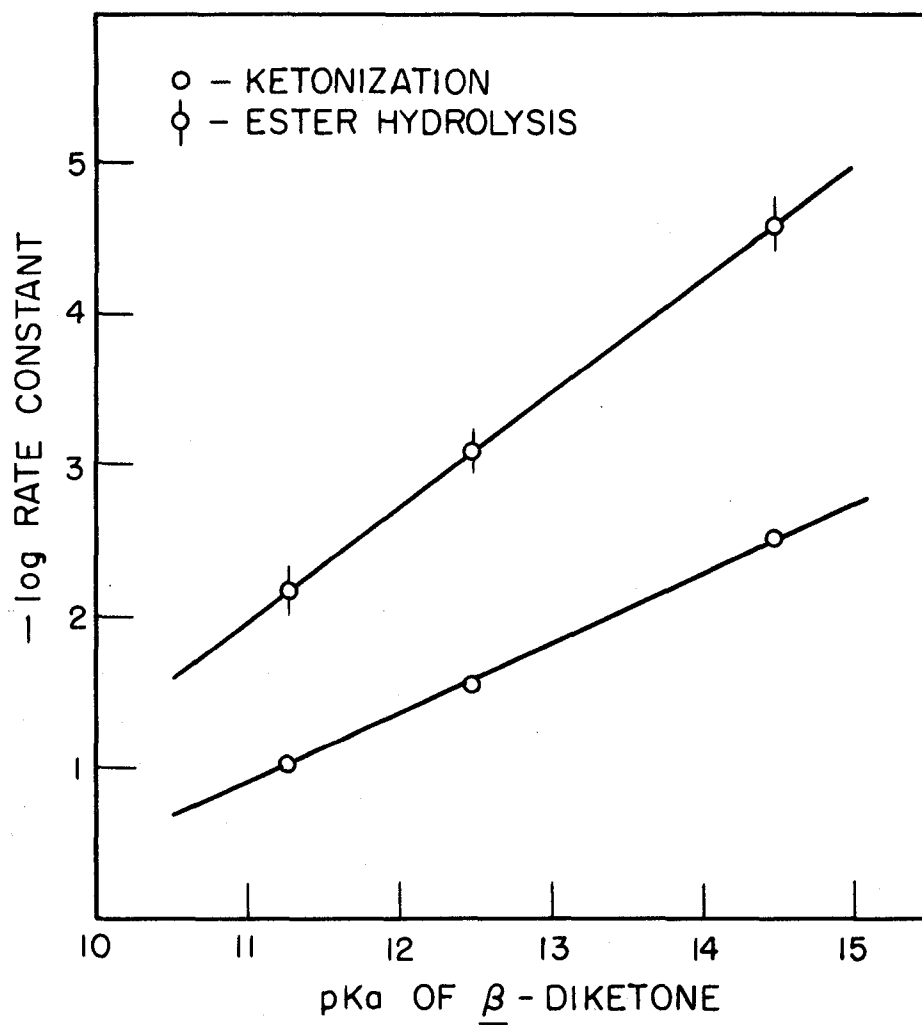


Figure 8

Correlation between Kinetic and
Equilibrium Data for beta-Diketones

whereas ester hydrolysis requires attack by the basic reagent on the carbonyl carbon, yet there is a direct relationship between the steric influences on the two reactions. Linear relationships such as those demonstrated here are not unusual in organic chemistry. However, no rigorous treatment has been given to them.

Formation Constants of Metal Chelates
of beta-Diketones

According to the argument presented in the historical section a plot of the first formation constant for a series of metal chelates of acetylacetone against the corresponding constants for the chelates of dipivaloylmethane or diisobutyrylmethane should not give a straight line. As the data of Irving (33) demonstrates, metal chelates of metals with high Edwards' beta values such as Cu(II) should deviate considerable from linearity; the deviation being in the direction of the more stable chelate. Plots of this type are given in Figures 9 and 10.

That $\log K_1$ for Cu(II) does not fall to the right of the line drawn indicates this constant is low for dipivaloylmethane and diisobutyrylmethane. A similar plot of $\log K_2$ shows that the second constant is much lower than would be expected for the two diketones since the point falls far to the left of the line.

Figure 9

Correlation between Formation Constants

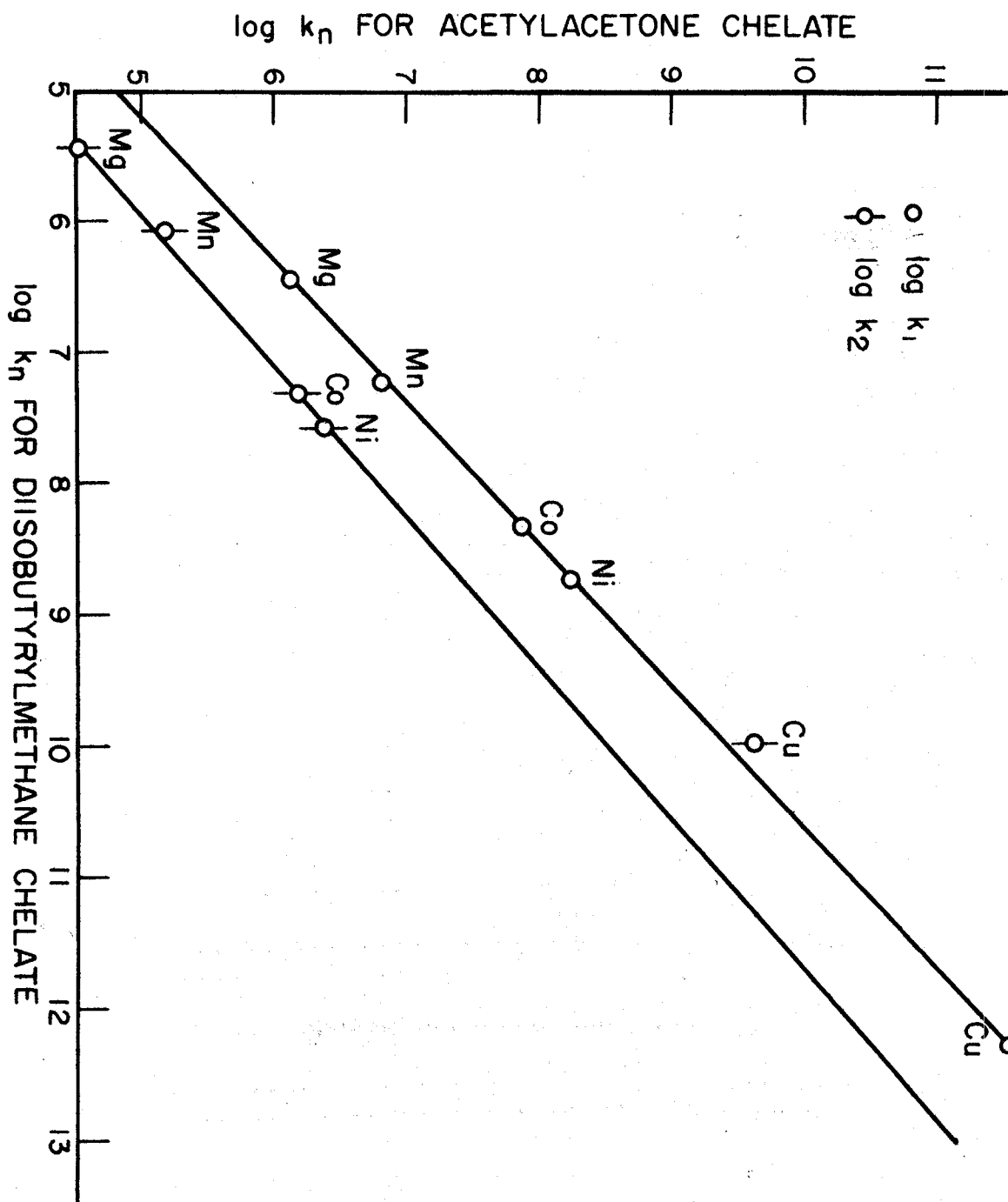
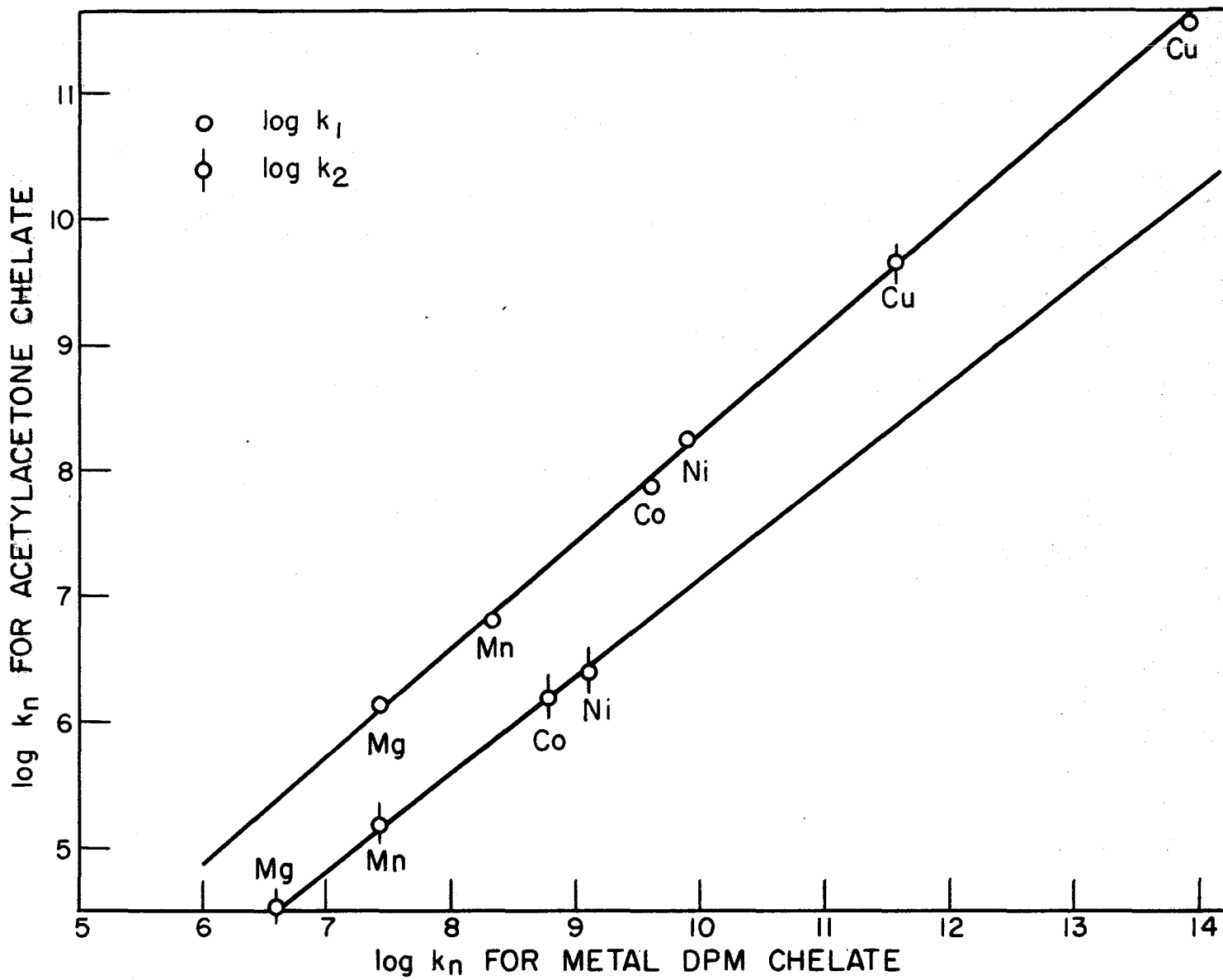


Figure 10

Correlation between Formation Constants



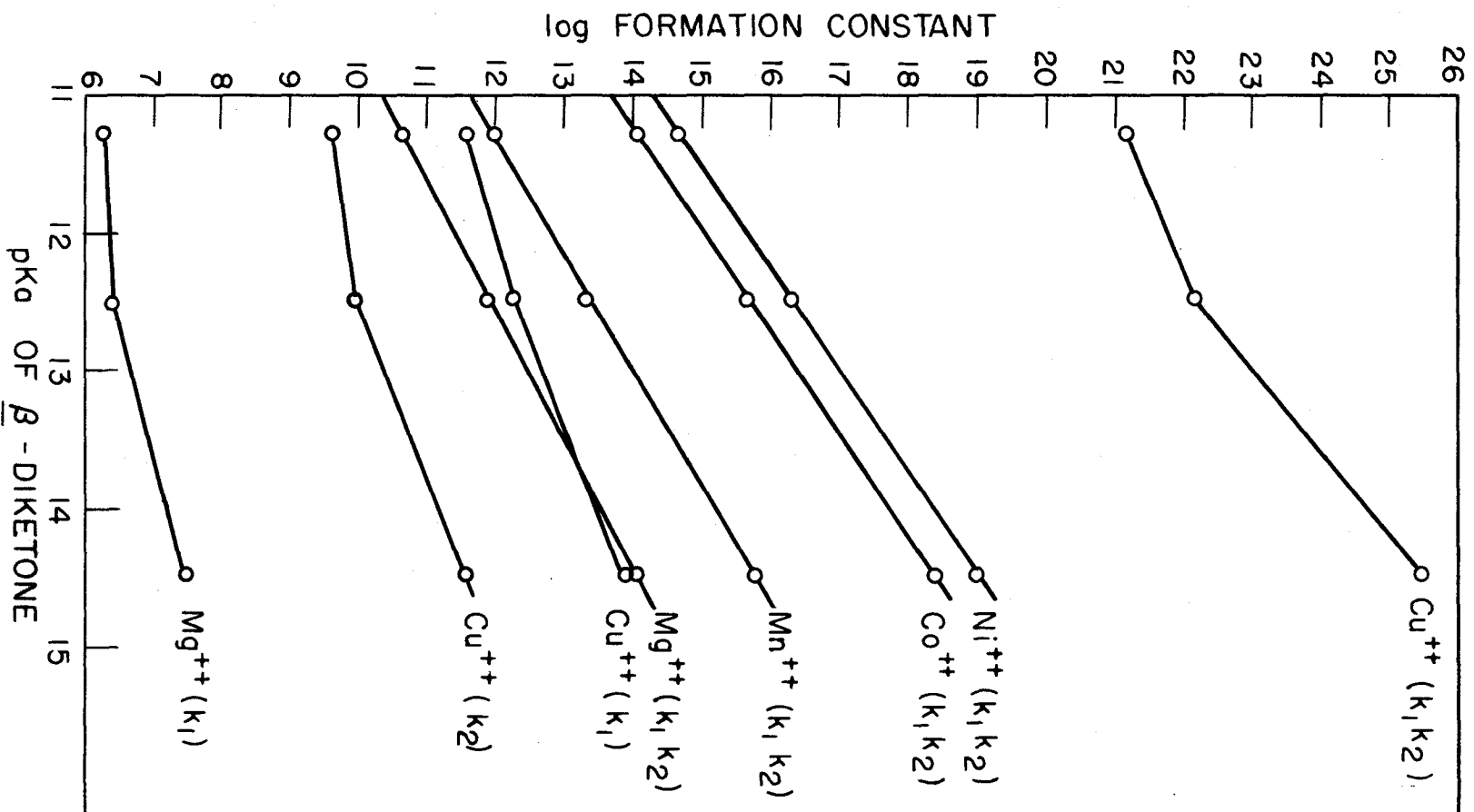
This evidence does not in itself constitute proof that both $\log K_1$ and $\log K_2$ are relatively low for Cu(II) since the beta values for the other metals are not given by Edwards. However, of the metals listed Cu(II) has the highest beta, which is about 1.5 times greater than the value for Zn(II).

The plot of \log formation constant against pK_a of the chelating agent as shown in Figure 11 reveals the low value for $\log K_1K_2$ for copper chelates of diisobutyrylmethane and dipivaloylmethane, but does not indicate $\log K_1$ for these chelates to be too low.

The copper chelate of acetylacetone has been shown to have a square planar configuration (42) and that of the nickel chelate is known to be tetrahedral (43). It is not likely that any of the other metals used in this study would form square complexes. If square complexes are formed from bulky ligands it is more probably that the effect of the bulk will be reflected in the formation constants than if a tetrahedral complex is formed. This appears to be the case with Cu(II) where the ^{minimum} steric effect is observed. Although a molecular model of the copper chelate of dipivaloylmethane does not show any steric hindrance between the two adjacent ligands, $\log K_1K_2$ appears to be low for this compound. Molecular models, however, cannot show to

Figure 11

Correlation of Formation Constants
with Basicity



what extent the ligand interferes with the solvation of the chelated metal. It is probable that both interference with solvation and between ligands contribute to the low formation constants.

Further evidence is shown by the relatively large separation factor for the copper chelates of the hindered reagents. If this is attributed to steric effects it is paradoxical to state that the abnormally small separation factor for the hindered chelates of the remaining metals is due to the same effect. However, when we consider that a tetrahedral configuration can tolerate greater steric requirements in the ligands it follows that the steric inhibition to solvation would become more important in determining the difference between the first and second formation constants. It thus appears that a monochelated metal is more acidic toward the second ligand when complexing with bulkier reagents due to the more effective removal of water of solvation. This effect is merely masked for copper by another steric effect.

Extraction of Lithium Ion by Dipivaloylmethane

The selectivity of dipivaloylmethane toward lithium may be attributed to two factors. The first is the small size of the lithium ion (0.60\AA) (44) as compared with the

sodium (0.95\AA) and potassium (1.33\AA) ions. It seems reasonable that if a proton can function as an efficient shield between the oxygens; any small positive ion may likewise form a shield (Structure IV). The inability to measure a formation constant for the sodium chelate in the same manner that the stability of the lithium chelate was measured clearly indicates the specificity for lithium. Differences in the structures between the lithium chelate and the sodium chelates are indicated in the infrared spectra (45).

The second factor which is closely related to the first is the desolvating powers of dipivaloylmethane. That ether was the only efficient solvent found indicates that the monochelated lithium ion still may solvate quite well, but the added organic bulk merely facilitates the displacement of water by ether. The factors influencing the solubilities of the alkali metal chelates of this reagent, and the changes which occur in absorption spectra with solvation are now under investigation (45).

SUMMARY

Evidence is presented which indicates that chelating ability may be greatly altered by changing the steric requirements of the ligand. A series of formation constants was measured for three beta-diketones. Thermodynamic values could not be obtained but relative concentration constants were. The constants obtained were correlated with each other and with the basicity of the reagent toward a proton. Each correlation indicated that the formation constants for the copper chelates of diisobutyrylmethane and dipivaloylmethane were low and exhibited large separation factors. However, relatively small separation factors were found for metal chelates which do not form square planar complexes.

A simple method for determining the extent of enolization of beta-diketones and the kinetics of enolization is presented. The method makes use of spectrophotometric measurements in the ultraviolet region. Correlations were observed between the pKa of the chelating agent, the kinetics of enolization, and the kinetics of hydrolysis of corresponding esters. Variations in the pKa and enol content were explained on the basis of steric effects.

A procedure for the separation of lithium from other alkali metal ions was developed, making use of the selectiv-

ity of dipivaloylmethane. The theoretical implications of this selectivity are discussed. Correlation of formation constants with a double basicity scale are reviewed. It is suggested that when using such correlations a chelate effect be taken into account. The application of the Edwards and Hammett equation to formation constants is discussed.

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