AN INVESTIGATION OF FAST LEWIS ACID-BASE REACTIONS BETWEEN COPPER(II) BIS(DIETHYLDITHIOCARBAMATE) AND HETEROCYCLIC BASES USING EPR SPECTROMETRY

by

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ABSTRACT

Fast Lewis acid-base reactions occur between square planar copper(II) complexes and weak organic bases in non-coordinating solvents. An example of such a reaction is that between copper(II)bis-(diethyl-dithiocarbamate), CuDDC, and a series of pyridines:

(1) CuDDC + pyridine $\rightleftharpoons$ CuDDC·pyridine

to form a five-coordinate adduct. Such an equilibrium can be treated as a two site exchange process using electron paramagnetic resonance (epr) spectrometry, with CuDDC the paramagnetic probe. The situation described by (1) is within the fast exchange approximation for epr.

In order to analyse line position epr data for reaction (1) the stoichiometry of the adduct must be established. Using plots of epr line position shift it was shown that CuDDC forms only 1:1 adducts with pyridine and the methyl-substituted pyridines studied. Knowing this stoichiometry the line position data was analysed using a least squares procedure to obtain the equilibrium, or binding, constant, $K$.

Linewidths were analysed as a function of base concentration to obtain the reverse rate constants, $k_r$, which were related to the forward rate constants using $k_f = K k_r$. Both equilibrium and rate constants were studied as a function of temperature using Arrhenius plots in order to obtain thermodynamic parameters. Temperature variations in the epr parameters were included in the analysis of the
Reaction (1) was studied with pyridine as the base in benzene, toluene, and chloroform. Enthalpies of reaction in the reverse direction increased in the solvent order given, and in the forward direction negative activation energies were observed, also increasing in the solvent order shown. Studies of several methyl-substituted pyridines in benzene showed a similar behaviour. An isokinetic relationship between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ was observed both for variation of solvent and of base. Such plots emphasise the dominant role solvent interactions play in reaction between neutral species in non-coordinating solvents.

The results obtained can be consistently and qualitatively interpreted in terms of a dynamic solvent structure reorganisation model proposed by Bennetto and Caldin, and are not adequately interpreted in terms of more traditional ideas.
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CHAPTER 1

INTRODUCTION

Magnetic resonance experiments in solids give results that can, in general, be considered as representative of static molecules. In solution, however, molecular motions, such as random Brownian tumbling, modulate the magnetic properties so as to narrow the observed line-widths and change the overall absorption lineshape. Also, chemical exchange processes, whereby there is a dynamic exchange between magnetically distinct sites, can lead to dramatic changes in magnetic resonance lineshapes. These effects occur because of a time-dependent averaging over the magnetically distinct sites and their magnetic properties, and are readily distinguished and analysed by magnetic resonance methods. For instance, if the exchange process is sufficiently rapid between the various sites, coalescence of the magnetic resonance signals will occur,
because of the uncertainty principle:

\[(1-1) \quad \tau \Delta \omega = \frac{1}{2\pi}\]

where \(\Delta \omega\) is the frequency separation of the corresponding resonance lines, and \(\tau\) the smallest time for which the separate sites can be distinguished. This time-averaging effect, under conditions of rapid exchange, leads to the site lifetimes becoming less than the critical value of \(\tau\) described by (1-1), and the signals are not resolvable.

Under these conditions, the time-averaged line positions and linewidths can be obtained and related to the dynamics of the exchange process, as was first shown by Bloembergen, Purcell, and Pound in 1948\(^2\).

Today there are available many procedures for analysing chemical exchange data for nuclear magnetic resonance (nmr) or electron paramagnetic resonance (epr) experiments\(^3\), covering all ranges from slow to fast exchange rates. For the study of rate processes, nmr and epr techniques complement each other, covering a range for first order processes of approximately 1 to \(10^{10}\) sec\(^{-1}\). Epr, in particular, is suitable for fast exchange studies, covering an exchange rate constant range of approximately \(10^5\) to \(10^{10}\) sec\(^{-1}\). The lower rate limit in magnetic resonance studies is that due to non-exchange contributions to the absorption linewidth. Linewidth and lineshape studies have been used in epr to obtain equilibrium and kinetic data for a large variety of reactions\(^3-6\). Ion association reactions\(^7-12\), electron-transfer reactions\(^13-16\), radical association-dissociation processes\(^17,18\), and ligand exchange\(^19,20\) have all been studied, the work referred to giving some useful or historically important examples.
Many ligand exchange processes are slow by epr criteria; rates being of the order of $10^3$ to $10^6$ sec$^{-1}$. Many exchange processes have been observed, the first probably being that of McGarvey$^{36}$, with a more detailed study of ligand exchange between Mn$^{2+}$ and various ligands in aqueous solution by Hayes and Myers$^{19}$. The first detailed work involving neutral species was reported by Walker et al$^{20}$ for the following equilibrium:

$$\text{VO(acac)}_2 + \text{pyridine} \rightleftharpoons \text{VO(acac)}_2 \cdot \text{pyridine}$$

where "acac" means acetylacetonate. This adduct formation equilibrium involves an exchange that averages both the g and hyperfine tensors, and the line broadening and hyperfine splittings were analysed to yield the rate constants $k_f$ and $k_r$ as $10^9$ mole$^{-1}$sec$^{-1}$ and $1.3 \times 10^7$ sec$^{-1}$ at 300°K, respectively. In general, any equilibrium of the kind:

$$\text{ML}_2 + B \rightleftharpoons \text{ML}_2 \cdot B$$

can be studied by magnetic resonance, using a two site analysis$^{3,4}$. The two site case is simplest and consequently most thoroughly analysed, but in principle any number of sites may be considered$^3$. In practice, computer techniques, although straightforward, become quite tedious for multiple site situations.

Aasa et al$^{21}$, in 1961, published details of linewidth effects and line position shifts in the epr spectrum of copper(II) bis(diethylidithiocarbamate) in benzene upon the addition of pyridine. Although not recognised by the authors as such, this was the first epr detection of fast ligand exchange for a transition metal system. When such Lewis
acid-base equilibria do occur under fast exchange conditions, the interpretation simplifies numerically. It is immediately apparent, at least in retrospect, that copper(II) bis(diethyldithiocarbamate), abbreviated to CuDDC from now on, undergoes weak complex formation with weak Lewis bases in non-coordinating solvents at a fast rate, and hence is a suitable paramagnetic probe upon which to perform ligand and solvent exchange epr studies.

Before continuing, it may be useful to note a few facts about CuDDC. CuDDC is a typical square planar copper(II) compound; copper(II) readily forming an unusually stable complex with salts of dithiocarbamic acid. Square planar copper(II) complexes have been extensively studied by epr, and a number of thorough reviews are available. Copper-nitrogen and copper-oxygen bonding complexes have been most commonly examined; relatively few stable copper(II)-sulfur complexes being reported until recently. In fact, copper complexes with sulfur-bonding ligands are usually more stable with the metal in the univalent state.

The crystal structure of CuDDC, a dark-green needle-like compound, has been determined, and the structure is schematically shown:

In the solid state, CuDDC exists as a bimolecular unit with copper-copper distance approximately 3.5 Å. This is close enough that spin-spin coupling between the copper atoms can be detected by epr. Mole-
cular weight determinations in benzene and chloroform solution, however, indicate that CuDDC exists in solution as a monomolecular unit.\footnote{31} It may be noted that the copper(II) atom is displaced out of the plane of the four sulfur atoms by 0.26 Å. Diethyldithiocarbamate complexes of Ag(II) and Au(II) have also been reported and investigated by epr.\footnote{29}

Hence a well-characterised, stable complex is available for ligand exchange studies. The quite large magnetic moment for copper(II) results in a favourable epr signal size for quite dilute solutions (10^{-4} M), which is useful for epr studies of kinetic processes. Further, and very important, epr spectra of CuDDC in solution are characterised by very narrow linewidths, which allows the experimentalist to distinguish between quite closely spaced epr signals. For the weak complexes formed by equilibrium processes such as those of (1-2) or (1-3), the X-band frequency separation is quite small: hence the fast exchange conditions. A suitable system for ligand exchange is thus available, and studies of CuDDC with various pyridines and in various solvents were carried out.

During the course of this work, two similar studies were published. One of these, by Corden and Rieger,\footnote{86} studied copper(II) bis(di-n-butyl-dithiocarbamate) in methylcyclohexane with pyridine, n-hexylamine, and piperidine. The fast and intermediate exchange results yielded rate and equilibrium constants. The latter work, however, neglected solvent and ligand effects to a large degree, and contained several important inconsistencies in the treatment of data, which can lead to large errors in the results. Similar criticism can be noted about the work of Shklyaev and Anufrienko\footnote{109} on CuDDC with pyridine in toluene. The incon-
sistencies will be discussed later, with an attempt to correct for them, and comparisons made with the results of this thesis. The methods used in both studies reported were similar to those used here.

Lately, much interest has surrounded the study of fast metal-complex reactions, mainly because little kinetic data has been obtained for metal ions that are highly labile with respect to substitution\textsuperscript{32,37}. In general, the purport of most of these studies has been to relate the findings to currently-held ideas about complexation and oxidation-reduction mechanisms. The nmr technique has been used to obtain much of the present data, particularly in aqueous solution. Much of the current interpretation is based on a proposal by Eigen\textsuperscript{21,33} that dissociative mechanisms dominate the kinetics to date, particularly for divalent transition metal ions\textsuperscript{32}. The experimental approach has been to study the rates of solvent exchange with respect to the stability constant, $k_o$, for formation of an outer-sphere complex; in terms of an observed rate, $k_{\text{obs}} = k_o k_f$:

$$\begin{align*}
M + L &\rightleftharpoons M,L \\
&\rightleftharpoons ML \\
\text{where all species are solvated, and } L \text{ can be solvent. } k_o \text{ can be estimated using the ideas of Fuoss and Eigen, as is excellently discussed in several articles}\textsuperscript{32,33,37}.
\end{align*}$$

Reactions of Ni$^{2+}$ in non-aqueous and aqueous solvents with various neutral bases led Bennetto and Caldin\textsuperscript{34} to propose a model involving a concerted rearrangement of solvent molecules to explain their results. The results obtained, they felt, were not consistent with ideas current-
ly held. In so far as current ideas are concerned, solvent and/or ligand exchange processes involve some sort of pre-equilibrium encounter to form an encounter complex. It can be readily shown that consideration of this model cannot adequately explain trends in activation energy due to specific solvent effects, particularly those observed in this work. The negative activation energies observed, in fact, rule out the possibility of any process that is dominated by inner-sphere complex formation, and hence involves breaking and/or reforming metal-ligand bonds. Bennetto and Caldin's concerted model does explain the results of this thesis in a consistent manner, and these results cannot be adequately explained otherwise. Objections by Rorabacher to the Bennetto-Caldin model for Ni\(^{2+}\) exchange processes, with the assertion that inner sphere effects can explain the results, may indeed be valid for that particular situation, but it seems clear that such ideas are insufficiently concerned with concerted solvent effects to explain very fast reactions between neutral substances in non-coordinating solvents.

The ideas necessary to obtain the necessary data for this work are considered in the next three chapters, followed by discussions of the results. Experimental details, which are quite standard, are felt not to contribute to the understanding of the mathematical methods used or the results obtained, and are therefore included at the end of the thesis.
CHAPTER 2

FAST EXCHANGE

A. AN INTRODUCTION: Magnetic resonance methods for measuring fast reaction rates have been applied to a considerable number of simple reactions. Although quite general treatments of the theories of magnetic resonance lineshapes for systems undergoing chemical exchange do exist, it is only with the use of large computers that full advantage can be made of such theories. Even where the computational facilities do exist, it may be advantageous to utilise more approximate, therefore simpler, procedures. This is the approach to be adopted here, but first a general outline of some pertinent details will be given.

Under conditions of no net chemical reaction, but where a definite chemical equilibrium has been established, there are likely to be sites of different environment which are magnetically distinguishable. Because
of the establishment of an equilibrium situation, an overall exchange between these environments, or sites, will occur. Magnetic resonance experiments are quite suitable for providing information about very fast reactions in such systems.

The intrinsic time scales of nmr and epr can be readily distinguished by noting that (classically) in a magnetic field of \( \approx 10,000 \) gauss (G) protons precess at about \( 10^7 \) Hz. and free electrons at about \( 10^{11} \) Hz. Considering that linewidth measurements are usually employed to obtain rate data from magnetic resonance experiments, any linewidths in excess of those caused by the spectrometer, and those caused by processes independent of chemical exchange, will give information on the rate process under investigation. Nmr spectrometers, for instance, have linewidths less than 1 Hz., and can be used to measure rates from about \( 10^{-1} \) to \( 10^6 \) sec\(^{-1} \) for diamagnetic systems. Epr methods have a practical lower limit of about \( 10^4 \) Hz. and thus rate processes over the range \( 10^5 \) to \( 10^{12} \) sec\(^{-1} \) may have observable effects in epr\(^{24} \).

It is instructive to note that since nuclei, and sometimes unpaired electrons, may have weak interactions with their environments, local environmental fluctuations will cause local magnetic field fluctuations which render the precessional frequencies of the nuclei (or electrons) time dependent\(^{24} \). This was mentioned briefly in chapter 1, and is caused by the equilibrium or rate process under study. If the rate is sufficiently fast compared to the difference in precessional frequencies of a nucleus (or electron) in the various local environments, then the nucleus will see only an overall magnetic field that is a time aver-
age of the various local fields. This is the fast exchange situation, and results ultimately in only a single resonance absorption, or line. Similarly, for slow exchange rates the nucleus will have time to process in each environment for a period long enough that several resonances due to each local field may appear. If local field differences are very small, then slow exchange processes may have observable effects on magnetic resonance spectra.

B. A BRIEF SURVEY OF LINESHAPE THEORIES: The physical description leading to all of the currently available lineshape theories in magnetic resonance is that first proposed by Bloembergen, Purcell, and Pound. In 1953 Gutowsky, McCall and Slichter gave the first method for the calculation of lineshapes in the presence of transfers between various magnetically distinguishable nuclei. In their study of relaxation effects they used the Bloch equations, suitably modified to account for nuclear transfers. Thus the so-called "modified Bloch equations" were used for the study of various chemical problems, and in 1958 McConnell presented a particularly simple derivation of these modified Bloch equations, with results identical to those of Gutowsky et al, for the case of low radiofrequency power and slow passage (nmr). These equations have been easily adapted to epr, and have been extended to describe the effects of rate processes on spin echo experiments. The spirit of McConnell's derivation was similar to that of Bloch's phenomenological description of nuclear relaxation in the sense that chemical exchange effects were incorporated simply as linear damping terms with coefficients related to the exchange rate.
A general theory of resonance absorption based on a transfer process being described in terms of Markoffian random modulation was derived by Anderson and Kubo\textsuperscript{44-46}. This theory gives formulae for the lineshape of a magnetic resonance spectrum directly, which can be used to obtain rate data, and is rather easily put into a convenient matrix form\textsuperscript{47}. Recently, Atkins\textsuperscript{48} has shown that the Kubo-Anderson-Tomita theory can also account for the fact that some spectra are superpositions of spectra and thus show an alternation of linewidth\textsuperscript{26}, but fails to account for non-secular contributions to the linewidth from degenerate magnetic resonance lines. This latter problem is common to Bloch equation methods and has led to the growing popularity of density matrix methods to describe lineshapes for systems where non-secular contributions may be important.

Non-secular transitions in magnetic resonance arise because of relaxation-induced transitions between spin states that are parallel and anti-parallel to the external magnetic field. In epr, for instance, the most important effects are usually the secular effects, or those involving no electron-spin transitions\textsuperscript{49} (adiabatic effects). The neglect of non-secular effects means that only motions that are not too rapid with respect to the Larmor frequency would be considered.

In principle, the density matrix methods have no limitations in exchange situations other than algebraic or computational, and are now routinely used. Bloch\textsuperscript{50,51} introduced a detailed treatment of magnetic relaxation within the framework of the density matrix formalism, using operator techniques, and an equivalent formulation by Redfield\textsuperscript{52}
is commonly used in epr, especially for description of the alternating linewidth phenomenon\textsuperscript{26,49,53}. One of the limitations of the Redfield-Bloch formulation is that because of certain approximations used to evaluate some integrals, the method is restricted to the region of motional narrowing of the lineshape. This is essentially because the evaluation of the integrals requires that the density matrix of the system not change much over the time period over which the integration is defined. A thorough discussion of this is given by Slichter\textsuperscript{54}, and by Abragam\textsuperscript{1}, who further gives an excellent account of an operator method for the calculation of magnetic resonance linewidths. Whereas the modified Bloch treatments are limited to secular contributions, but not limited to any exchange rate range, the Redfield theory is limited to the fast motion region, but can be readily generalised to include all transitions contributing to any resonance spectrum.

Kaplan\textsuperscript{56-58} and Alexander\textsuperscript{59}, using an exchange operator to describe the effects of exchange on the density matrix for any system\textsuperscript{56,57}, describe a density matrix method that is not restricted to any rate region, and which can include non-secular transitions. Binsch\textsuperscript{60} has extended these ideas to obtain a general density matrix formalism, suitable for application to intermediate exchange rate situations where computational facilities exist. The spirit of Alexander's modification to the equation of motion for the density matrix is the addition of phenomenological terms to account for intra- and inter-molecular exchange, and terms to account for the non-exchange contributions to the lineshape. Thus there is a resemblance to the modified Bloch
equations, to some extent. In fact, the results of the density matrix treatments are essentially quantum mechanical equivalents to the modified Bloch equations, and in the limit of fast exchange, for instance, the results are identical\textsuperscript{24}. The recent modifications to the Kaplan-Alexander theory by Kaplan\textsuperscript{58} and Binsch\textsuperscript{60} also allow for intramolecular conversion where it is difficult to explicitly define an exchange operator of the sort used for hindered internal rotation. Examples of the use of various density matrix methods for several problems have been published for both nmr and epr exchange studies\textsuperscript{61-63}.

To end this rather brief survey of lineshape theories, mention should be made of a treatment of chemical exchange mentioned by Anderson et al\textsuperscript{64-66}, similar in concept to Sillescu's more general treatment\textsuperscript{67}. In these treatments, molecular reorientation is related to a fluctuating environment (for example, chemical exchange) using probability theory, and the effects upon the molecular motion by the fluctuating process can be described in terms of rotational correlation functions of the molecules and a probability function describing the fluctuations. In principle, these ideas can be extended to any exchange process.

C. THE BLOCH EQUATIONS: Before proceeding to outline the treatment of chemical exchange used in this thesis, it is useful to sketch the development of the phenomenological equations proposed by Bloch to describe the behaviour of nuclear magnetic moments in external magnetic fields. For complete details as to the validity of these equations, the papers by Bloch\textsuperscript{39,50,51} should be consulted.
In a system of weakly interacting spins, Bloch postulated that the magnetization vector per unit volume, \( \mathbf{M} \), obeys the equation:

\[
\frac{d\mathbf{M}}{dt} = \gamma (\mathbf{M} \times \mathbf{H})
\]

where \( \mathbf{H} \) is the external magnetic field vector and \( \gamma \) the magnetogyric ratio. By simply adding relaxation forces to (2-1) phenomenologically it is possible to describe the behaviour of an isolated group of spins. By resolving \( \mathbf{H} \) into components such that \( H_0 \) is in the z direction, and such that a perpendicular (to z) modulating field \( H_1 \) is acting to cause the magnetic resonance, one obtains:

(2-2)

\[
\begin{align*}
H_0 &= H_z \\
H_x &= H_1 \cos \omega t \\
H_y &= -H_1 \sin \omega t
\end{align*}
\]

where \( \omega \) is the angular frequency of rotation of \( H_1 \) about \( H_0 \).

By adding the rotating terms to the steady state solutions for the motion of \( \mathbf{M} \) in a static field \( H_0 \) the Bloch equations follow:

\[
\frac{dM_x}{dt} = -\frac{M_x}{T_2} + \gamma (M_y H_0 + M_z H_1 \sin \omega t)
\]

(2-3)

\[
\frac{dM_y}{dt} = -\frac{M_y}{T_2} + \gamma (M_z H_1 \cos \omega t - M_x H_0)
\]

\[
\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1} + \gamma (M_x H_1 \sin \omega t + M_y H_1 \cos \omega t)
\]

where the first terms in each line are those due to relaxation in a static field \( H_0 \), \( T_2 \) being the transverse or spin-spin relaxation time,
and $T_1$ the longitudinal or spin-lattice relaxation time, $M_0$ the equilibrium magnetization in the $z$-direction. $T_1$ clearly governs the rate of approach of the magnetization to an equilibrium value upon the application of a magnetic field. Similarly, $T_2$, usually different from $T_1$, governs the decay of phase coherence of spins in the $xy$ plane, or is the time taken by the spins to dephase once they are in phase. In a liquid, the many rapid fluctuations in local fields (it is these local fields that cause the dephasing of the spins: if the range of these small fields is $\delta H$ then the spins will dephase in a time $T_2 \sim (\delta H)^{-1/2}$ during the rotation of a molecule whose spin(s) is(are) precessing at the Larmor frequency will mean that these small local effects are averaged out, and that $M_x$ and $M_y$ will decay in the same manner as $M_z$. Thus $T_1 = T_2$. Quantitatively, if some time $\tau$ describes the time for molecular rotation, for example, the rapid fluctuations (compared to the Larmor frequency, $\omega_0$) are such that:

\[(2-4) \quad \omega_0 \tau \ll 1\]

and hence $T_1 = T_2$. Chemical exchange effects can also interrupt the phase coherence of spins at the Larmor frequency by causing sudden changes in the precession frequency, and this situation would be manifest by change in $T_2$, but not in $T_1$. Under these conditions, $T_2 < T_1^{69}$.

The Bloch equations may be simplified by transforming from the fixed laboratory Cartesian axis system to a set of axes rotating
with the applied field $H_1$, where the transformation is described by:

$$
M_x = u \cos \omega t - v \sin \omega t
$$

$$
M_y = -u \sin \omega t - v \cos \omega t
$$

Substituting (2-5) into (2-3), and rearranging, gives:

$$
\frac{du}{dt} + \frac{u}{T_2} + (\omega_o - \omega)v = 0
$$

$$
\frac{dv}{dt} + \frac{v}{T_2} - (\omega_o - \omega)u + \gamma H_1 M_z = 0
$$

$$
\frac{dM_z}{dt} + \frac{(M_z - M_o)}{T_1} - \gamma H_1 v = 0
$$

At steady state, $M_z$ is constant and the transverse components of $M$ rotate with $H_1$; therefore setting the time derivatives to zero yields:

$$
u = M_o \frac{\gamma H_1 T_2^2 (\omega_o - \omega)}{1 + T_2^2 (\omega_o - \omega)^2 + \gamma H_1^2 T_1 T_2}
$$

$$
v = -M_o \frac{\gamma H_1 T_2}{1 + T_2^2 (\omega_o - \omega)^2 + \gamma^2 H_1^2 T_1 T_2}
$$

$$
M_z = M_o \frac{1 + T_2^2 (\omega_o - \omega)^2}{1 + T_2^2 (\omega_o - \omega)^2 + \gamma^2 H_1^2 T_1 T_2}
$$

In most magnetic resonance experiments, $H_1$ is chosen to be small ($\gamma H_1 \ll \gamma H_o$), therefore the last term in the denominators of (2-7) can be neglected since $\gamma^2 H_1^2 T_1 T_2 << 1$. This latter condition
further implies that $M_z \sim M_o$. Incorporating this approximation into (2-7) yields a Lorentzian form for the lineshape components:

$$u = -\frac{\gamma H_1 T_2 M_o (\omega_o - \omega) T_2}{1 + (\omega_o - \omega)^2 T_2^2}$$

$$v = -\frac{\gamma H_1 T_2 M_o}{1 + (\omega_o - \omega)^2 T_2^2}$$

(2-8)

and as $(\omega_o - \omega) T_2$ varies from $-\infty$ to $+\infty$ the resonance absorption goes through a maximum at $\omega_o = \omega$. The Lorentzian form of the lineshape equation resulting from (2-8) is a limitation of the Bloch treatment, since many lineshapes, especially in solids, are not well-approximated by such a function. For spectra obtained for samples in solution, however, the observed lineshapes are often quite well described by a Lorentzian lineshape.

D. **MODIFIED BLOCH EQUATIONS AND FAST EXCHANGE:** McConnell's modifications to the Bloch equations to allow for reversible chemical exchange processes give the same results as the earlier work of Gutowsky et al., but because the notation is simpler, only McConnell's treatment will be outlined here.

Returning to eqs. (2-6) and recalling that if $H_1$ is small then $M_z$ does not change significantly from $M_o$, the first two equations may be written:

$$\frac{du}{dt} + \frac{u}{T_2} + \frac{(\omega_o - \omega)v}{T_2} = 0$$

(2-9)
Defining a complex magnetic moment $G_j = u_j + iv_j$, and a complex frequency of
\[ \alpha_j = \frac{1}{\tau_j} - i(\omega_j - \omega), \]
where $j$ refers to the spin site under consideration, the time dependence of $G_j$ can be
written:

\[ \frac{dG_j}{dt} + \alpha_j G_j = -i\gamma H M_{oj} \]

Now, if an exchange process is occurring between the $j$ sites, then McConnell proposed that this can be described by assuming that all spins be considered to remain in one site until they perform a sudden "jump" to another site. It is assumed that no spin precession occurs during the jump (clearly the sites must be magnetically distinct for the exchange to have an effect). For a spin at some site $j$, it is further assumed that there is a constant probability per unit time, $1/\tau_{jk}$, of the spin jumping to site $k$. This is the same as if site $k$ becomes site $j$ because of the exchange process, with the spin remaining at the original site $j$. Since the fractional populations of all the sites must sum to unity:

\[ \sum_j p_j = 1 \]

Consideration of a detailed-balancing scheme suggests that:

\[ p_j \sum_k \frac{1}{\tau_{jk}} = \sum_k p_k \frac{1}{\tau_{jk}} \]
where \( 1/\tau_{jk} \neq 0 \) if \( j \neq k \), and \( \sum_k 1/\tau_{jk} \) is the probability per unit time of the spin at site \( j \) going to some other site \( k \). Thus by adding on an appropriate exchange term to (2-10) the Bloch equations can be readily modified to include chemical exchange. For transfers of moments, \( G_j \), between \( j \) sites the result is:

\[
\frac{dG_j}{dt} + \left[ \alpha_j G_j - i\gamma H_{1M}^{O_j} + \sum_k (\tau^{-1}_{kj} G_k - \tau^{-1}_{jk} G_j) \right] = 0
\]

The steady state solution may be obtained by setting the time derivative of \( G_j \) equal to zero, solving the resulting linear equations for \( G_j \) and taking the imaginary part of \( G = \Im G_j \), since the intensity of absorption is proportional to the imaginary part of \( G \).

For many equilibrium situations, and in particular those studied here, only two distinct sites are involved in the exchange process. Although in principle it is easy to include any number of sites, in practice it will be accompanied by a great deal of algebra. For the two site case, it is convenient to label the sites \( A \) and \( B \), whence the fractional populations of each site, \( p_A \) and \( p_B \), will be related to the site lifetimes (inverse of total probability of a jump from that site to the other) as follows:

\[
p_A = \frac{\tau_A}{\tau_B + \tau_A} = 1 - p_B
\]

and the modified Bloch equations are:

\[
\frac{dG_A}{dt} + \alpha_A G_A = -i\gamma H_{1M}^{O_A} + \tau^{-1}_B G_B - \tau^{-1}_A G_A
\]
By defining \( p_{A,M}^{O} = M_{O} \), and solving (2-15) for steady state conditions, one obtains:

\[
(2-16) \quad G = G_A + G_B = -i\gamma H_{1,0}^{M} \frac{\tau_A + \tau_B + \tau_A^{-1} \tau_B^{-1} (\alpha_{A} + \alpha_{B})}{(1 + \alpha_{A}) (1 + \alpha_{B})} - 1
\]

Solutions to (2-16) can be obtained over any range of \( \tau_A \) and \( \tau_B \), although a particularly simple result is obtained if \( \tau_A = \tau_B \), suitable for fast computer methods\(^{24}\). The complete evaluation of (2-16) will not be considered here, but is available in standard texts, for example that of Pople, Schneider and Bernstein\(^{68}\), and references therein.

Two limiting cases of (2-16) are commonly used to interpret temperature-dependent magnetic resonance spectra; the slow and fast exchange limits.

Slow exchange criteria are satisfied when the separation of the precessional frequencies of the two sites A and B, \((\omega_A - \omega_B)\), is large compared to the inverse of the lifetimes in either site A or site B. Under this condition the magnetic resonance absorption will consist of two lines at \( \omega_A \) and \( \omega_B \), and because these signals are considered to be completely separated, the assumption is made that when the frequency \( \omega \) is close to \( \omega_A \), \( G_B \) is effectively zero. And vice-versa. Thus:

\[
(2-17) \quad G \sim G_A \sim -i\gamma H_{1,0}^{M} \frac{P_{A} \tau_A}{1 + \alpha_{A} \tau_A}
\]
with an imaginary part:

\[(2-18) \quad v = -\gamma H_1 M_0 \frac{P_A T_A^{1}}{1 + (T_A^{1})^2 (\omega_A - \omega)^2} \]

i.e. a signal centered at \(\omega_A\) with linewidth

\[(2-19) \quad T_A^{1-1} = T_A^{2-1} + \tau_A^{-1} \]

where \(T_A^{2-1}\) is the linewidth in the absence of exchange. If \(T_A^{2-1}\) is known, a series of spectra over a known temperature range, in the slow exchange region, will give a series of \(\tau_A^{-1}\) values from (2-19) for the process. In this region, care must be taken not to include spectra where there is any significant overlap of signals.

For very fast exchange processes, such as those to be discussed in this thesis, the appropriate approximation to Bloch's equations are obtained when \(\tau_A\) and \(\tau_B\) are short compared to the reciprocal of the precessional frequency differences:

\[\tau \ll (\omega_A - \omega_B)^{-1} \]

where \(\tau = \tau_A \tau_B / (\tau_A + \tau_B)\) is a mean lifetime. In this limit one can obtain:

\[(2-20) \quad G = -i\gamma H_1 M_0 \frac{\tau_A + \tau_B}{\alpha_A \tau_A + \alpha_B \tau_B} = -i\gamma H_1 M_0 \frac{\tau_A}{\alpha_A \tau_A + \alpha_B \tau_B} \]

by using (2-16) and (2-15). Separating the imaginary part yields:

\[(2-21) \quad v = -\gamma H_1 M_0 \frac{T_2}{1 + T_2^2 (P_A \omega_A + P_B \omega_B - \omega)^2} \]
where $T_2^{-1}$ is the mean linewidth of a signal centered at the mean frequency:

\[(2-22) \quad \langle \omega \rangle = p_A \omega_A + p_B \omega_B \]

\[T_2^{-1} = p_A T_2A + p_B T_2B \]

Usually the region of complete narrowing in which the observed linewidth is a simple weighted mean as in (2-22) is not reached, and the signal is subject to lifetime broadening caused by the fact that the exchange process is not quite fast enough to satisfy $\tau << (\omega_A - \omega_B)^{-1}$. Such lifetime broadening can be taken into account by substituting $\langle \omega \rangle$ from (2-22) into (2-16), and expanding in powers of $\tau$ to give:

\[(2-23) \quad T_2^{-1} = p_A T_2A + p_B T_2B + p_A^2 p_B^2 (\tau_A + \tau_B) (\omega_A - \omega_B)^2 \]

This equation can be used to give information about rate processes from fast exchange spectra if significant lifetime broadening is present.

Now, a bimolecular rate process can be described by the following:

\[(2-24) \quad A + L \xrightarrow{k_A} B \]

where $k_B = T_B^{-1}$, and since $K = k_A / k_B$, $k_A = K k_B$. The explicit ligand dependence of $k_A$, whereas $k_B$ is a simple first order rate constant, suggests that numerical analysis of line broadening using (2-23) can be simplified if the term in $\tau_A + \tau_B$ is replaced by a term in
For a reaction that is first order in both directions, it is unimportant which rate is analysed. It should be made clear that \( k \) can be obtained from (2-23), as will be detailed in the next chapter, and this is, in fact, all that the line position data alone can yield about the rate process. Hence, using (2-14) one can write:

\[
(2-25) \quad p_B = \frac{\tau_B}{(\tau_A + \tau_B)}
\]

Hence:

\[
(2-26) \quad \tau_B = (\tau_A + \tau_B)p_B
\]

Substituting (2-26) into (2-23) eliminates \( (\tau_A + \tau_B) \) and gives the useful result:

\[
(2-27) \quad T_2^{-1} = p_A T_2A^{-1} + p_B T_2B^{-1} + p_A^2 p_B \tau_B (\omega_A - \omega_B)^2
\]

Under certain conditions modifications may be made to (2-27) to extend its application to even slower rates, hence broader lines, by considering more terms in the method of Meiboom et al. These modifications are not large, however, and do not change the ideas involved.

In using the fast exchange approximation it must be noted that the two lines involved in (2-22) must not be resolvable, and the linewidths in the absence of exchange must be small compared to the rate of exchange. This latter condition is easily met in this work, but a more general form of (2-27) that is not restricted is
obtainable if necessary\textsuperscript{24}. Thus the conditions imposed by the fast exchange approximations may be conveniently summarised as:

\[ \tau \left| \omega_A - \omega_B \right| < 1 \]
\[ \tau \left| T^{-1}_{2A} - T^{-1}_{2B} \right| < 1 \]
\[ \tau \left( T^{-1}_{2,0} \right) < 1 \]

where \( T^{-1}_{2,0} = p_A T^{-1}_{2A} + p_B T^{-1}_{2B} \). Knowing the experimentally-determined line positions, (2-22) can be used to obtain equilibrium constants, \( K \), and the frequency difference, \( (\omega_A - \omega_B) \), from a least squares fit of \(<\omega>\) to the base concentration. These treatments are detailed in chapters 4 and 9. Potential difficulties that can invalidate the results obtained for \( K \) and \( k_1 \) are outlined next, before a more detailed treatment of the linewidths is presented.
A. **INTRODUCTION:** The determination of formation, or equilibrium, constants, and other thermodynamic parameters for weak complexes has been the subject of some controversy\(^{71-74}\), with many authors in the past putting undue confidence on unreliable data\(^{73}\). Person\(^ {74}\) outlined the problem by noting that the most accurate values of a formation constant are obtained when the concentration of the complex being formed (an adduct, for example) is approximately the same as the unbound concentration of the most dilute component. In epr terms, the most dilute component is invariably the paramagnetic substance, and thus Person's warning suggests that epr measurements of formation constants should bracket \(p_A = p_B = 0.5\) (in terms of nomenclature introduced in chapter 2). Equivalently, the mole fractions
of species A and B should be equal. The nmr situation for chemical shift measurements is restricted similarly, although with respect to those species giving rise to nmr signals, but it may often be impossible to achieve the necessary conditions if $K$ is very small ($< 1 \text{ M}^{-1}$) or very large ($> 10 \text{ M}^{-1}$), or if solubility problems, for instance, prevent attainment of a suitable concentration range.

In epr studies, the very high sensitivity (one can detect $\sim10^{12}$ spins for a typical free radical) means that quite low concentrations ($\leq 10^{-4} \text{ M}$) can be used, and hence solubility problems are not usually serious.

If experimental formation constant data are assembled, in order to determine if some reaction model is operative, certain anomalies may occur because the data are not collected over a sufficiently wide concentration range. To ascribe any meaning, therefore, to such data invites repudiation of the results at a later date by an experimentalist working in a different concentration range. Such instances have been reported, for instance, for some nmr studies of hydrogen bonding in solvents. It is essential, therefore, to decide before assembling the data what conditions should be fulfilled. Surprisingly, this has not been the case often enough in the estimation of formation constants from spectroscopic methods.

B. **THE SATURATION FRACTION:** To introduce the ideas wanted without undue complication, the weak molecular complex to be formed will be
considered to have 1:1 stoichiometry with respect to the reactants. Thus the system to be considered is:

\[
\begin{align*}
(3-1) && A + L & \xrightleftharpoons{k_f \over k_r} B; \quad K = k_f / k_r \\
\end{align*}
\]

Specifically, the copper(II)bis(diethylthiocarbamate) "reaction" with various pyridines is representable in terms of (3-1) as

\[
\begin{align*}
(3-2) && ML_2 + B & \rightleftharpoons ML_2B \\
\end{align*}
\]

Formation constants are generally obtained by keeping the dilute component, A, fixed and "titrating" it by the addition of varying amounts of L, in a suitable solvent. Thus in terms of eq. (3-1) the formation constant is defined by the expression:

\[
\begin{align*}
\end{align*}
\]

where \([A_o]\) and \([L_o]\) are the fixed concentration of A and the total concentration of L, respectively.

As \([B]\) varies from zero to, in principle, \([A_o]\), a useful fraction of the complex, B, can be expressed as the saturation fraction, s:

\[
\begin{align*}
(3-4) && s = [B]/[A_o] = K[L]/(1 + K[L]) \\
\end{align*}
\]

where 0 ≤ s ≤ 1.

The definition in (3-4) is thus the binding probability discussed by Weber.76 Person's requirement for maximum confidence in K can be expressed in terms of (3-4) as s = 0.5, thus \([L] = 1/K\).
Tacit in the definitions used so far is that all solutions are ideal, and hence activity coefficients are unity, thus enabling the use of molar concentration in determining $K$. The solutions generally used are obviously not ideal, and to be correct one should write:

$$K' = \frac{a_B}{a_A a_L} = \frac{[B]}{[A][L]} \cdot \frac{\gamma_B}{\gamma_A \gamma_L} = KK'$$

where $a_i$ are the activities of the various entities in the solvent being used, and $\gamma_i$ are the corresponding activity coefficients.

Thus if the solutions are non-ideal, the real equilibrium constant, $K'$, is defined as in eq. (3-5),; and not the equilibrium quotient $K$. Determination of $K'$ is, however, difficult since data are not available for many solvent systems.

C. **CONSIDERATION OF POTENTIAL ERRORS**: It is often possible to arrange conditions experimentally such that the concentration of the adduct, or complex, is almost negligible in comparison to the concentration of the excess ligand (base). In an epr experiment this situation is realised very easily, since the maximum concentration of the adduct is that of the unadducted metal compound (for a case similar to the one being considered in this work) which is always very small compared to the base concentration. Therefore substitution of $[L] \approx [L_o]$ can be made, with an associated error

$$\varepsilon = \frac{K - K_t}{K_t} = -s[A_o]/[L_o]$$
where $K$ is the value deduced from setting $[L] \sim [L_o]$, and $K_t$ the true value of the equilibrium constant, where $[L] = [L_o] - [B]$. Because $\varepsilon$ is always $< 0$, its value should be very small (considerably less than experimental error) for the neglection of $[B]$ to not affect the determined value of $K$. This error is not a statistical error and must therefore be considered with some care. In the epr experiments performed here the value of $[A_o]/[L_o]$ is always $< 5 \times 10^{-3}$ and often is $< 10^{-4}$. Since $s$ must $< 1$, $\varepsilon$ in these experiments is certainly negligible within experimental error of $K$, which is $\sim + 5\%$.

To determine the minimum error arising in the determination of $K$ under situations in which it is not possible to separate $K$ easily from some concentration (of base) - dependent parameter (such as optical absorbance, chemical shift, or line position shift) Weber\textsuperscript{76} derived the formula, assuming the usual propagation of errors:

\[
\varepsilon = \frac{\Delta K}{K} \approx \Delta s \left[\frac{1}{s^2} + \frac{1}{(1 - s)^2}\right]^{1/2}
\]

which is interesting in that it depends upon $s$ alone, and thus gives an example of the usefulness of using the concept of the saturation fraction. The derivation of (3-7) also assumes that errors in $[L_o]$ and $[A_o]$ be small compared to the error in $s$.

A plot of $\varepsilon/\Delta s$ vs. $s$ shows\textsuperscript{71,76} that the most accurate values of $K$ will be obtained when $s$ lies between about 0.2 and 0.8.
Deranleau proceeded further, and using information theory derived the result that \( s \) has a maximum information content of 83% at \( s = 0.76 \). In particular, the region \( 0 < s < 0.1 \), although containing 10% of the saturation curve, contains only 4% of the information content. Increasing the number of measurements in this region does not alter this situation, since the information content is a ratio of theoretically accumulated to total available information, \( (I/I_{\text{max}}) \). In fact, the rate of accumulation of information with respect to \( s \) is:

\[
\frac{I}{I_{\text{max}}} = 1 + s \ln s + \frac{1}{s} \ln(1 - s)^2 \ln(1 - s)
\]

The preceding remarks are not intended to give an authoritative discussion of experimental validity but only to point out that in order to test any stoichiometric model of weak complex formation equilibrium constants the maximum amount of accurate information must be obtained. That information is available in the saturation factor region approximately bounded by \( 0.2 < s < 0.8 \). Unfortunately much data has been accumulated in the region \( 0 < s < 0.2 \), as illustrated in Table I of reference 73, which means that \( K \)'s determined from such data are unreliable. It is also noteworthy that much of the optical spectroscopy work on weak molecular complexes with Lewis bases has been performed at very low \( s \) regions.

If it is impossible, because of experimental limitations, to satisfy the criteria set by Deranleau and Person, then
an experimental model may be examined using other sources to improve the results that are available.\footnote{72}

D. PRESENTATION OF DATA: Once the question of a suitable concentration range over which to study some reversible process has been established, then a suitable presentation of the data can be made. The information required may be direct or indirect. For instance, the fast exchange situation between two supposed sites may be interpreted using epr data in terms of a two-site model (1:1 binding, say). It would be useful, therefore, to use the ideas of this section to decide upon a means of verifying 1:1 binding without recourse to any but experimentally-determined results. Once 1:1 binding has been, or has not been, established, then the results can be interpreted in terms of the 1:1 model, or some other, respectively.

In the case of the present work, parameters available from some plot (in addition to the properties of the plot itself) could also be used to check the results obtained from analysis of the epr data; which was in this case obtained for a 1:1 binding model.

The first problem to consider is that for weak complexes $K$ must be known in order to evaluate the saturation fraction, $s$ (eq.(3-4)). Clearly at some point $K$ must be used to obtain $s$ unless an independent method of measuring the amount of complexed material is available. By noting that $s$ can be replaced with a
useful experimental parameter, a significant plot may still be obtained.

In an epr experiment, the position of a fast exchange line position for a particular system represents an average according to (2-22). Rearranging (2-22) one obtains:

$$\langle \omega \rangle - \omega_A = p_B (\omega_A - \omega_B)$$

and defining $\delta = \langle \omega \rangle - \omega_A$, $\delta_0 = \omega_B - \omega_A$ yields:

$$\delta = p_B \delta_0$$

but it has been shown previously that $p_B = s$, hence:

$$s = \delta / \delta_0$$

Using these definitions of $\delta$ and $\delta_0$ for epr gives the same equation for $s$ as for the nmr case, where $\delta$ is the observed chemical shift, and $\delta_0$ the shift of pure complex.

Now, to expand $p_B$ in eq.(3-10) in terms of some experimentally measurable or known parameters would avoid the problem of having to know $\delta_0$, and further allow the presentation of "raw" data to determine the stoichiometry of complex formation.

Thus first the equilibrium constant for the 1:1 process defined by eq.(3-1) is:

$$K = \frac{[B]}{([A] - [B])([L] - [B])} = \frac{k_f}{k_r}$$
Now, as mentioned earlier \([L_o] \gg [A_o]\), hence \([L_o] \gg [B]\).

Therefore (3-12) becomes:

\[
(3-13) \quad K = \frac{[B]}{([A_o] - [B])[L_o]}
\]

Further, \(p_A = \frac{\tau_A}{\tau_A + \tau_B} = 1 - p_B\), and \(\tau_B = 1/k_r\), \(\tau_A = 1/k_f[L_o]\)

\[
(3-14) \quad p_A = \frac{1}{1 + K[L_o]} \quad p_B = \frac{K[L_o]}{1 + K[L_o]}
\]

Substituting into eq. (3-10) gives:

\[
(3-15) \quad \delta = \frac{K[L_o]}{1 + K[L_o]} \quad \delta = K[L_o](\delta - \delta)
\]

Since \([L_o]\) is known and \(\delta\) can be obtained experimentally (there are important considerations about the determined \(\delta\) that will be considered later, involving the definition of \(\omega_A\)), it is possible to plot the relationships shown in (3-15) in several ways.

To satisfy the Deranleau-Person criteria, and hence to plot all the theoretically obtainable data, covering the complete \(s\) range, both origins of any suitable plot must be included. This is to unequivocally determine the quality of the curve. Reciprocal plots such as the Benesi-Hildebrand (1/[\(L_o\)] vs. 1/\(\delta\)) or half-reciprocal plots such as the Scott (\([L_o]/\delta\) vs. \([L_o]\)) are open-ended on the abscissa, allowing the experimentalist to vary the concentration \([L_o]\), and hence the range of \(s\), in a man-
ner that can often give a straight line simply by distorting low s points with uneven s spacing\textsuperscript{71}. Normal errors in small concentration values in the reciprocal plots will become very large errors and thus render such points almost valueless.

The higher concentration points, although becoming progressively more reliable, tend to be crowded together. Thus it has been suggested that in order to obtain most confidence in plotting (3-15), for the purpose of deciding whether the plot is linear or not, reciprocal-type plots be avoided\textsuperscript{71}.

Plots based on the Bjerrum formation function\textsuperscript{79} (s vs. log[L\textsubscript{0}]) are curved and symmetrical about s = 0.5 for 1:1 binding, and thus give, in addition to a complete range of the saturation fraction, an easily-recognized plot symmetry for the correct model. A simpler, linear, plot of experimental data giving reliable confirmation of stoichiometry and a presentation of the whole s range is the Scatchard plot\textsuperscript{80}. This is simply a plot of δ/[L\textsubscript{0}] against δ, and one can see from (3-15), by dividing by the constant δ\textsubscript{o}, that this plot is equivalent to one of s/[L\textsubscript{0}] vs. s. This plot will be linear, with well-spaced points, over a suitable range of saturation fraction if the data is correct for the model chosen. Clearly, this plot can be used to obtain estimates for the formation constant and δ\textsubscript{o}, since it has slope - K and intercept Kδ\textsubscript{o}. In this work, Scatchard plots of the experimental data were used to establish
stoichiometry, and the values of $K$ and $\delta_o$ available from the slope and intercept used only to check the results of least squares fitting procedures. The only exception to this was for the reaction of CuDDC with 2-methylpyridine in benzene, where the least squares fits were inconclusive because of the very small values of $K$ ($0.02 \leq K \leq 0.08$). The Scatchard plots were linear and a reasonable set of values of $K$ and $\delta_o$ obtainable. These results, and the others, are detailed in chapter 5.

Some questions as to the concentration-scale dependence of values of $K$ and $\delta_o$ obtained from Scatchard, Scott, or Benesi-Hildebrand plots clearly do not affect the present work, since the plots were used mostly to check linearity. It is worth noting, however, that recent publications suggest that the concentration-dependence can be removed by correct interpretation of the equation to be used. In other words, differences in $K$ and $\delta_o$ values obtained by Hanna and Rose for concentration scales in molal, molar, and mole fraction do not arise if donor non-ideality is taken into account.

E. **MULTIPLE EQUILIBRIA:**

a) **The binding model:** The Scatchard presentation was chosen for this work because it satisfies the requirements of both convenience and accuracy. A linear Scatchard plot generally confirms the model proposed as long as the saturation fraction range is at least seventy five percent covered. In the
case of competing or multiple equilibria, for example, small saturation fractions invariably give straight line plots, although the slopes and intercepts will be different for each case. Also, various combinations of formation constants for several consecutive equilibria can also give rise to linear relations, add it will be shown in this work that this possibility must be considered.

Rather than attempt to give a general treatment, which is not particularly difficult but involves considerable algebra, the case to be considered will be that of the possibility of formation of both 1:1 and 1:2 adducts. Chemically, this case has a large number of applications, and can be conveniently applied to divalent copper. Although there are strong stereochemical and spectroscopic arguments for stating that square-planar copper(II) compounds, such as CuDDC, do not form stable 1:2 adducts with weak bases in solution, the discussion is quite useful.

The complex formation process is to be described by the following model:

\[ (3-16) \quad \begin{array}{c}
A \xrightleftharpoons{K_1} B \\
\xrightarrow{K_2} C
\end{array} \]

where for a metal complex, ML₂, interacting with a Lewis base, B:

\[ (3-17) \quad ML₂ + B \xleftrightarrow{K_1} ML₂B \]

\[ ML₂B + B \xrightarrow{K_2} ML₂B₂ \]
This model assumes, for CuDDC specifically, that no formation of \( \text{ML}_2 B_2 \) is attained directly by the addition of two molecules of base of \( \text{ML}_2 \) in a simultaneous process.

For epr purposes there is generally no need to restrict the relative rates of formation and dissociation of B and C, in (3-16).

However, by restricting the model to the fast exchange region the requirement will be that all rates are sufficient to maintain overall fast exchange conditions. This allows some simplification as in the two site equilibrium model that describes 1:1 formation, and hence an obvious extension to (2-22) can be made, since:  

\[
\langle \omega \rangle = \sum_i p_i \omega_i .
\]

Hence, for the three site case described by (3-16), one may write:

\[
\langle \omega \rangle = p_A \omega_A + p_B \omega_B + p_C \omega_C
\]

At equilibrium, it is possible to define the \( p_i \) in terms of the base concentration as in the two site case, again requiring \([L] = [L_0]\). Hence:

\[
[B] = K_1 [A][L_0] \]

\[
[C] = K_2 [B][L_0] = K_1 K_2 [A][L_0]^2
\]
Defining \( T_C = [A] + [B] + [C] \) results in:

\[
P_A = \frac{[A]}{T_C}
\]

(3-21)

\[
P_B = \frac{K_1[A][L_0]}{T_C}
\]

\[
P_C = \frac{K_1 K_2[A][L_0]^2}{T_C}
\]

or, using (3-19):

(3-22)

\[
T_C \langle \omega \rangle = [A] \omega_A + K_1[A][L_0] \omega_B + K_1 K_2[A][L_0]^2 \omega_C
\]

but \( T_C = [A] + K_1[A][L_0] + K_1 K_2[L_0]^2[A] \) from (3-20), hence:

(3-23)

\[
\langle \omega \rangle = \frac{\omega_A + K_1[L_0] \omega_B + K_1 K_2[L_0]^2 \omega_C}{1 + K_1[L_0] + K_1 K_2[L_0]^2}
\]

Thus the effects of two competing equilibria can be readily determined from (3-23) for any values of \( \omega_1 \) and \( K_1 \) and \( K_2 \), over a suitable base concentration range.

b) Presentation and evaluation of data: As with the 1:1 binding situation discussed earlier, there are several means of presenting the line position data for an equilibrium process to determine if multiple equilibria are present to any extent. Also, as before, reciprocal and half-reciprocal plots have the disadvantage of being dependent on the region of the saturation curve over which data is collected. In general, it has been shown, both by Deranleau \(^{71}\) and by eq.(3-23) that any of the plots considered previously will be curved. The most curved
plot will be the Scatchard plot, where $\frac{\delta}{[L_0]}$ vs. $\delta$ is plotted, since no reciprocal effects will distort the axes. The data collected in this work for a series of $\omega_1$ values and $K_1$ and $K_2$ being consistent with the present experiment, show that the Scatchard plots are indeed curved (see Chapter 5). Some exceptions occur when $K_2 < K_1$.

It is again important to note that Scott or Benesi-Hildebrand plots made on restricted regions of the saturation fraction scale (high or low regions, especially) are often quite linear, even when a plot over the whole s range is quite curved. This effect is even apparent for the extremes of the Scatchard-type plot. Deranleau's second paper,$^{71}$ on multiple equilibria, shows convincing evidence of the fact that only if a significant percentage ($> 75\%$) of the saturation fraction is measured should any confidence be placed in the results. Even then, special, or circumstantial, combinations of multiple equilibria parameters may result in linear plots. In these situations, checks can be made over a range of expected or known results to see if, indeed, such cases can occur. This was done in the present work, and the results are available in chapter 5.

Finally, the question of possible competing equilibrium processes reemphasises the uncertainty of using isosbestic points, as in absorption spectroscopy, as proof (or not) of a specific number of species being present. Combined with some other form of confirmation, however, the use of isosbestic
points can be very informative. It could arise, for instance, that for two competing equilibria $K_1 = K_2$ and the absorbtivities of $A$, $B$, and $C$; $a_i$, are all equal. Under these conditions all plots of data considered previously will be linear, and the absorption spectrum will show an isosbestic point. This argument holds for any number of equilibria as long as the $K_i$ and $a_i$, respectively, are equal. This result has been obtained in a different context, and is admittedly rather unlikely to occur, but is included only to demonstrate that often very little care has been taken to unequivocally establish that only 1:1 binding is present. In fact, as noted by Person and Deranleau, few, if any, of the weak complex formation processes studied spectrophotometrically have been proved to be 1:1 complexes, where pertinent, unless they were isolable and amenable to chemical analysis.
CHAPTER 4

INFORMATION FROM THE LINewidth

A. RELATIONSHIP OF THE LINewidth TO KINETICS: In the limit of extreme narrowing of a magnetic resonance line, the fast exchange limit, no information about the rate of exchange is available. The linewidth in this limit is:

\[ T_2^{-1} = p_A T_{2A}^{-1} + p_B T_{2B}^{-1} \]

and \( p_A = 1 - p_B = \tau_A / (\tau_A + \tau_B) = (1 + K[L_o])^{-1} \), using the notation developed in chapters 2 and 3. In epr studies of exchanging systems, the limit of fast exchange (\( k > 10^{10} \) sec\(^{-1} \)) is rarely reached, and lifetime broadening contributes to the observed linewidth:

\[ T_2^{-1} = p_A T_{2A}^{-1} + p_B T_{2B}^{-1} + p_A^2 p_B^2 (\tau_A + \tau_B)(\omega_A - \omega_B)^2 \]
For the present study, where the equilibrium process is defined by:

\[(4-3) \quad \text{CuL}_2 + B \xrightarrow{k_f} \text{CuL}_2B\]

\(k_f\) can be equated with \(\tau_B^{-1}\), and \(k_f = Kk_r\). Thus, as noted earlier, it is more convenient to rewrite (4-2) as:

\[(4-4) \quad T_2^{-1} = p_A T_{2A}^{-1} + p_B T_{2B}^{-1} + p_A p_B T_B (\omega_A - \omega_B)^2\]

Before considering the non-exchange linewidths, \(T_{2A}^{-1}\) and \(T_{2B}^{-1}\), in more detail, it should be noted that the fast exchange conditions (2-28) necessary to obtain (4-4) are often not met. For narrow epr lines, the linewidth conditions are usually satisfied, but the line separation condition, \(\tau |\omega_A - \omega_B| \ll 1\) can easily be unsatisfied. For the reaction of CuDDC with pyridines in benzene, for instance, \(\tau (\omega_A - \omega_B) \sim 0.8\) for some temperatures. Of course, \(\omega_A - \omega_B\) is intimately related to the formation constant, and as the temperature is decreased, it is noted that \(\omega_A - \omega_B\), and hence \(K\), increases. Clearly, the fast exchange conditions will be violated for a certain value of \(K\), no matter what the temperature. In this work, it appears that \(K\) must be \(< 2\). Corden and Rieger\(^8\) found similar limitations in their work, and to overcome these they expanded the modified Bloch lineshape function in terms of frequency and linewidth to include extra "near fast exchange" terms for the linewidth:
(4-5) \[ T_2^{-1} = p_A T_{2A}^{-1} + p_B T_{2B}^{-1} + \frac{p_A p_B}{\tau} \left\{ (\Delta^2 - \delta^2) + (p_A - p_B) \delta (3\Delta^2 - \delta^2) \right\} \]

where \( \delta = \tau (T_{2A}^{-1} - T_{2B}^{-1}) \), \( \Delta = \tau (\omega_A - \omega_B) \), \( r = \tau / (p_A T_{2A}^{-1} + p_B T_{2B}^{-1}) \), and \( \tau = \frac{\tau_A \tau_B}{\tau_A + \tau_B} \). Equation (4-5) was shown to effectively allow values of \( \tau(\omega_A - \omega_B) \) as large as 0.5 - 0.8, hence extending the fast exchange approximation to slower rates than (4-4), when certain of the terms \( \delta, \Delta \) or \( r \) become large. The inclusion of the extra terms as in (4-5) is usually not necessary in the present work, but where the exchange rate becomes slightly slower, but not slow enough to cause a separation of the lines, the extra terms can become quite large.

B. NON-EXCHANGE LINELWIDTHS: For studies of exchange processes by magnetic resonance, knowledge of non-exchange linewidths is usually necessary. It is usually assumed that the non-exchange linewidths, measured under some condition wherein it is assumed no exchange processes are taking place, define the components of the exchanging system equally as well as the non-exchanging one. It is often assumed, also, that the non-exchanging linewidths are temperature-independent. This is rarely, if ever, the case, and such variation should be taken into account. Similarly for viscosity effects, etc.. Two methods commonly prevail for the measurement of non-exchange linewidths. One is to measure the line-
widths of the separated lines in the limit of very slow exchange (i.e. at low temperatures), and the other is to measure the line-widths of the individual species separately in the absence of exchange conditions. In the former method, the temperature-dependence of the non-exchange widths is obscured by the exchange process, and only in solids is it likely to be a useful method. In solids, the assumption can often be made that the only temperature-dependent contribution to the linewidth is that of the exchange process. The second method for measuring $T_2^{-1}$ and $T_2^{-1}$ does enable the temperature-dependence of the non-exchange linewidths to be observed. For instance, dissolving a metal complex in neat solvent and measuring its temperature dependence in the absence of another solvent or ligand is quite straightforward. However, this latter method suffers from difficulty in being able to define the "end-points" A and B, in solution. The value of A is ideally defined in terms of a completely non-coordinating environment, and B in terms of a completely co-ordinated environment. In solutions, the solvent effects alone render the achievement of these end points experimentally difficult. The approximation that A be defined as the A species in a non-coordinating solvent is, however, a reasonable one for some solvents. It is never possible, however, to obtain 100% co-ordination of some ligand to A in a fast equilibrium process, since the self-concentration of the ligand is usually $< 20 \text{ M}$. Hence the value of B obtained from neat ligand solutions may be subject to uncertainty. It
is useful to keep this in mind when considering fast exchange processes in solution.

It is possible, however, to avoid these difficulties with an appropriate least squares technique, by using the solvent and ligand measurements of A and B as good approximations to $\omega_A$, $\omega_B$, $T_{2A}^{-1}$, and $T_{2B}^{-1}$. By allowing the least squares routine to vary over these parameters, as well as $k$ and $\tau_B$, respectively, independent end-points can be obtained, which can then be compared with those measured. This is the procedure used in this work, and is described in more detail in chapter 9.

Non-exchange epr linewidths in solution have a temperature dependence defined approximately by the properties of the liquid. Liquid structure fluctuations and collisions, as well as molecular vibrations, give rise to a modulation of electric fields experienced by a nucleus or electron attached to some molecule, and this may cause relaxation. For the doublet state of an ion Kivelson has investigated three major electronic relaxation processes: the direct and Raman processes of Van Vleck, and the Orbach process. In the direct process a spin flip (absorption of energy) occurs through absorption of a phonon of energy equivalent to the energy required for the flip, whereas in the Raman process spin flips are caused by phonons of arbitrary energy with the emission of phonons with appropriate energy. The Orbach process involves absorption of a phonon of equivalent
energy, as in the direct process, but involves a simultaneous electronic excitation, hence the overall absorption of energy is higher than in the direct process. These mechanisms were originally proposed for the solid state, and are discussed in more detail by Van Vleck and Orbach. Kivelson was able to show that none of these electronic relaxation processes is very important in liquids, in comparison to other effects there, although the Orbach process can, in favourable circumstances, be significant. Overall, in fact, it is difficult to separate such electronic relaxation processes from rotational effects, since it is often difficult to study a suitable \( S=\frac{1}{2} \) system over a wide enough temperature range, in a liquid, in order to distinguish the various effects. If the temperature range required was available, however, the electronic and rotational relaxation effects could, in principle, be readily separated since they all have different temperature coefficients. Kivelson has developed equations describing these temperature relationships.

Specifically, \( \text{Cu}^{2+} \) ions (\( d^9 \), equivalent to \( S=\frac{1}{2} \)) have very much larger rotational relaxation effects in solution than electronic effects. The rotational, or tumbling, contributions to the linewidth give rise to an \( m_1 \)-dependence (\( m_1 \) is the nuclear spin quantum number in the field direction) which is, in turn, temperature dependent. This \( m_1 \)-dependence was first interpreted in terms of a randomly-tumbling microcrystal by McConnell, and
the description was later extended by McGarvery\textsuperscript{36}, for several transition metal ions. In effect, the random tumbling of the microcrystal is insufficient to average out the anisotropy in the $g$- and $A$-tensors of the central ion, and these incompletely-averaged terms can be shown to contribute to the linewidth. For states of higher multiplicity, anisotropy in the zero-field splitting is generally a predominant contribution to the solution linewidths\textsuperscript{26,91,92,103}.

The most comprehensive treatment of the effects of tumbling on epr lineshapes has been given by Kivelson et al\textsuperscript{91,92}. Important extensions to this work were developed by McLachlan\textsuperscript{93} and others\textsuperscript{94,103} in addition to those references mentioned in chapter 2, and the ideas overlap considerably with the work of Kivelson, which is based on the Kubo-Tomita-Anderson approach.

The results are best summarised in terms of the peak-to-peak linewidth (sec$^{-1}$), $\Delta H$, and the $m_I$ values a particular ion may take ($-I \leq m_I \leq +I$, $I$ the nuclear spin):

\begin{equation}
\Delta H(m_I) = \alpha' + \alpha'' + \beta m_I + \gamma m_I^2 + \delta m_I^3
\end{equation}

where:

\begin{equation}
\alpha' = (\tau_C/360)(g_o \beta \pi \sqrt{3}/h)^{-1} \left\{ 8(g_o \Delta \delta)^2 [4 + 3(1 + 2 \omega o^2 \tau_C^2)^{-1}] + 9I(I+1)b^2 [3 + 7(1 + 2 \omega o^2 \tau_C^2)^{-1}] \right\}
\end{equation}

\begin{equation}
\beta = (\tau_C/15)(g_o \beta \pi \sqrt{3}/h)^{-1}bH_o \Delta \delta [4 + 3(1 + 2 \omega o^2 \tau_C^2)^{-1}]
\end{equation}
\begin{align}
\gamma &= \left(\frac{\tau_C}{40}\right) \left(\frac{g_o \beta \mu_0 / 3}{h}\right)^{-1} \left[5 - \left(1 + \omega_o \frac{2}{\tau_C^2}\right)^{-1}\right] b^2 \\
\delta &= \left(\frac{\tau_C}{100}\right) \left(\frac{g_o \beta \mu_0 / 3}{h}\right)^{-1} \left(b^2 a_o / (\hbar \omega_o)\right)
\end{align}

and the following definitions are used:

\begin{align}
b &= 2(A_U + 2A_L) / 3h, \quad \Delta \delta = (g_\parallel - g_\perp) \beta / h \\
a_o &= 1/3(A_U + 2A_L), \quad g_o = 1/3(g_\parallel + 2g_\perp).
\end{align}

The usual epr nomenclature is used. (4-7) is for an axially-symmetric \( g \) and hyperfine tensor, which is quite common for transition metal ions, and can be easily generalised to an anisotropic case.\(^9\)\(^6\) It may be noted that the term \( (\frac{g_o \beta \mu_0 / 3}{h})^{-1} \) is the conversion from peak-to-peak (derivative) linewidth to \( T_2^{-1} \), the inverse of the true transverse relaxation time defined by the half-width at half-height of the absorption line.\(^9\)\(^5\) The rotational correlation time, \( \tau_C \), is that time required for a molecule tumbling in solution to regain an initial orientation with respect to its environment. The term \( a'' \) in (4-6) is a \( \tau_C \)-independent term containing all contributions from sources such as spin-rotational relaxation, dipole-dipole relaxation, etc.\(^9\)\(^8\) The form of (4-7) given is an approximation requiring \( a_o / \omega_o \) be very small, where \( \omega_o \) is the centre of the epr spectrum. Including this term generates various cross terms discussed by Wilson and Kivelson,\(^9\)\(^6\) which may contribute as much as fifteen percent to the linewidth under certain conditions (especially
when \( \tau_C \sim \omega_0 \). The exact form of (4-6) and (4-7) is not important here; what is important is that the \( m_1 \)-dependence of the linewidth is shown explicitly.

The terms \( \alpha, \beta, \gamma \) and \( \delta \) take the form of complicated functions of the inner products of the \( g- \) and \( A- \)tensors, with the linear coefficient, \( \beta \), containing a mixed tensor product, \( g:A \).

Figure (4-1) shows \( m_1 \)-dependences in vanadyl and cupric ion epr spectra. Since the coefficient \( \delta \) is usually small, spectra in which \( \gamma \) dominates will be symmetric, with respect to the center, and spectra with \( \beta \) dominating will show marked asymmetry, broadening from one side to the other. Copper(II) \( \beta \)-diketonates (fig. 4-1) and CuDDC are good examples of this asymmetry. Since hyperfine splittings are often more sensitive to temperature than \( g \) values for transition metal chelates, the observed linewidths may show marked temperature effects indicative of increasing symmetry as temperature increases. Of course, \( \tau_C \) will also decrease as viscosity decreases and this will have some effect in addition to the changes just described.

Temperature dependence of the various coefficients in (4-7) is in \( \tau_C \) and epr parameters. It is usually assumed, however, that the hyperfine terms are temperature-independent; values of \( b \) and \( \Delta \gamma \) being obtained at 77°K in a frozen liquid, for example, and used for all temperatures. This is not necessarily a good assumption unless made over a small temperature
Vanadyl Acetylacetonate at X-band in Toluene (236 K)

VOAcac at K-band in Toluene (297 K)

CuAcac at X-band in chloroform (331 K)

CuAcac at K-band in chloroform (300 K)

Fig 4-1: $M_z$-dependence of Linewidths
range, since hyperfine splittings in solution are quite strongly temperature dependent. It is difficult to avoid the assumption, though, since very few systems have been studied from very low temperatures to room temperatures in order to evaluate the temperature effects.

Thus, assuming temperature-independent hyperfine parameters, all the temperature variation is in $\tau_C$. Values for the rotational correlation time are usually calculated from the Debye theory of rotational relaxation for a rotating sphere:

$$\tau_C = \frac{4\pi n r^3}{3kT}$$

where $\eta$ is the bulk viscosity of the solvent at some temperature $T$, $r$ the radius of the sphere, and $k$ the Boltzmann constant.

Values of $r$ obtained from calculations of $\tau_C$ by means other than (4-8), however, are usually considerably smaller than the molecular diameter of the compound being studied$^{104}$. This effect has been corrected for by Kivelson et al.$^{105,106}$ by introducing an empirical parameter, $\kappa$, which is unity when Debye theory holds. A quite accurate method of evaluating $\tau_C$ appears to be that of Burlamacchi$^{104}$, who used the fact that the linewidth passes through a maximum at $\omega_0\tau_C = 1$ as the viscosity is increased, for ions possessing zero-field splitting.

In conclusion, there must be a temperature dependence of the non-exchange linewidths in an exchanging system, defined according to the preceding remarks. The various coefficients were not calculated in this work, since they add nothing to the under-
standing of the basic exchange process; the non-exchange line-
widths were simply measured as a function of temperature, in-
corporating all non-exchange effects implicitly.

C. ROTATIONAL EFFECTS AND EXCHANGE: As shown in the preceding
section, for transition metal ions the dominant contributions
to the linewidths are the anisotropies in the g and hyperfine
tensors, coupled to the random (Brownian) diffusion of the
metal ion complex. Spin rotational terms are also important,
and can be shown to depend on a term $T/\eta$, which can be most
conveniently included in non-concentration-dependent terms.
It is assumed here that the only concentration dependence is
the contribution of any exchange process, and indeed a simple
test for the presence of an exchange process is a dependence
on concentration.

An exchange process will modify the rotational behaviour
of the complex by superposing an additional modulation on the
components of the anisotropic g and A tensors. In general the
relative times $\tau_C$ and $\tau_{ex}$, for reorientation of the complex
and exchange with another complex, respectively, can be shown
to be critical in the determination of lineshapes. The
mathematical treatment of the two competing processes has been
described in some detail using reorientation probabilities
coupled with Redfield theory, but the most applicable
treatment for the present case is that of Atherton and Luckhurst\textsuperscript{100}. An outline of the treatment follows to illustrate the effects expected.

The time-independent Hamiltonian describing the two site situation can be represented as a weighted sum, much as the Bloch lineshapes were:

\begin{equation}
\mathcal{H} = \langle g \rangle HS_z + \langle a \rangle I.S
\end{equation}

where $\langle g \rangle = p_A g_A + p_B g_B; \langle a \rangle = p_A a_A + p_B a_B$ and where non-secular terms are not included.

The time-dependent Hamiltonian can be written:

\begin{equation}
\mathcal{H}(t) = \mathcal{H}_1(t) + \mathcal{H}_2(t)
\end{equation}

\begin{equation}
\mathcal{H}_1(t) = \beta (g(t) - \langle g \rangle) HS_z + (a(t) - \langle a \rangle) I.S
\end{equation}

\begin{equation}
\mathcal{H}_2(t) = \beta H g_{\alpha \beta}(t)S_{\beta} + I_{\alpha A \beta}(t)S_{\beta}
\end{equation}

where $\mathcal{H}_1(t)$ arises from modulation of the isotropic parts of the $g$ and $A$ tensors; $\mathcal{H}_2(t)$ from modulation of anisotropic tensors. The tensor convention of summing automatically over repeated subscripts is used in $\mathcal{H}_2(t)$.

In $\mathcal{H}_1(t)$, $g(t)$ and $a(t)$ are randomly fluctuating between $g_A$ and $g_B$, and $a_A$ and $a_B$, respectively, whereas in $\mathcal{H}_2(t)$ rotation of the complex and ligand exchange give rise to a more complicated temporal behaviour. Atherton and Luckhurst found it expedient to evaluate the scalar terms from $\mathcal{H}_1(t)$ and the
second-rank tensor terms from $\mathcal{H}_2(t)$ separately. Since $S=1/2$ transition metal ions have no degenerate allowed epr transitions, the relaxation matrix can be readily interpreted in terms of the exchange contributions to the linewidth$^{1,100}$. The pure exchange (scalar) contribution is:

$$T_2^{-1} = \frac{4\Delta g^2 B^2 H^2}{16\pi} \frac{1}{T_A + T_B} + 2\Delta g \Delta a \frac{H}{1 + \omega^2 \tau^2} \left\{ \text{non-secular terms} \right\}$$

Equation (4-11) is simply the Bloch equation (4-2) expanded to first order in $\omega$ ($\equiv g_i B_i / \hbar + a_i m_i$), plus non-secular contributions.

The evaluation of the contribution to the linewidth from $\mathcal{H}_2(t)$ is not straightforward, and involves probability theory to determine the effects of a random jump between sites, and Brownian motion of the complex itself. These contributions can be conveniently summarised$^{100}$ to show that the total linewidth is simply that due to ligand exchange plus the weighted mean of the non-exchange linewidths, $T_2^{-1}$. As in (4-11) this is simply the Bloch result plus non-secular terms. As will be shown later, the non-secular terms, calculated from (4-11) are very small ($< 0.5\%$ usually, often $<< 0.5\%$) for the exchange process studied in this thesis, but were included for completeness.
The non-secular tumbling terms will become important, and thus invalidate the Bloch treatment, when $\tau_C$ becomes comparable to $\tau$, or even slower than $\tau$. The $\tau_C$ dependence here is involved in the $H_2(t)$ terms, which are not explicitly shown. This limit, $\tau \ll \tau_C$, thus represents a limitation to the applicability of the Bloch equations for exchange process in a liquid medium. The density matrix methods\textsuperscript{1,56-60}, and those of Anderson and Sillescu\textsuperscript{64-67} provide means for including all regions of $\tau_C$ relative to $\tau$. A microscopic analysis of the contributions of $\tau$ and $\tau_C$ to motional narrowing of magnetic resonance lines\textsuperscript{101} has shown that exchange-narrowed and motional-narrowed lines can be separated by the Fourier transforms of the various correlation functions contributing to the lineshape. This is specifically important when a line narrowing is present that is not clearly defined to be exchange- or motionally-narrowed.

In general, since rotational correlation times are much shorter than most exchange times, the Bloch equations will provide unambiguous and relatively simple interpretations of the exchange process, as long as any motional effects are included in the non-exchange linewidths. In particular, transition-metal complexes reacting reversibly with various ligands to form specific adducts give epr spectra which can often be analysed using the modified Bloch equations.
CHAPTER 5

THE SYSTEM: EXPERIMENTAL RESULTS

A. LEAST SQUARES ANALYSIS OF THE RESULTS: The electron paramagnetic resonance spectrum of copper(II) bis(diethyldithiocarbamate) in a non-coordinating solvent is typically that shown in fig. 5-1a. The effects of chemical exchange, caused by the presence of pyridine at 1 M concentration, are typified by fig. 5-1b. As can be seen the asymmetry of the benzene spectrum can be removed by the chemical exchange contributions to various lines.

Dependence of the line position and linewidth on pyridine concentration for benzene/pyridine mixtures at 300°K is illustrated in figs. 5-2 and 5-3. Agreement between experimental (circles) and least-squares (solid lines) results is
Fig 5-1a: CuDDC in benzene (300 K)
Fig 5-1b: CuDDC in 1M pyridine in benzene (300 K)
Fig 5-2: Concentration dependence of average line position in benzene-pyridine solution (300 K)
Fig 5-3: Concentration dependence of linewidth in benzene-pyridine solution. (300 K)
well within experimental error. The maxima in the linewidth plots are caused by the lifetime broadening contributions to the fast exchange linewidth, and give an empirical evaluation of the exchange rate: the slower the rate, hence the larger $\tau_B$ becomes, the higher the maximum. The position of the maximum, with respect to base concentration, can be readily shown to be at $[L_o] = (2K)^{-1}$, since the lifetime broadening contribution is proportional to $p_{A}^{2}p_{B}$, from (4-4), which has a maximum at $p_A = 2/3$, and $p_A = (1 + K[L_o])^{-1}$.

The least squares fitting routines were allowed to vary over the end points ($\omega_A$ and $\omega_B$, or $T_{2A}^{-1}$ and $T_{2B}^{-1}$) as well as the quantity of interest, $K$ or $\tau_B$. As noted in more detail in chapter 9, the procedure obviates the need to use neat solvent measurements for the end points, and thus the fitted values of $\omega_A$ and $\omega_B$ could be associated with solvent-free parameters. This is developed more fully in the next chapter, but for now it can be stated that all least squares-fitted values of the end points are not necessarily the same as those measured in neat solvents. The trends with temperature are preserved, however, and all results were found to be quite consistent internally.

In other words, parameters from the line position data were used without change in the linewidth analyses, allowing all data to stand, or fall, on their own merit. Several authors
have not been able to obtain consistent results without applying constraints, however, and it would seem that this must be due to the data and/or method of analysis. Tables 5-1 and 5-2 give a complete description of the data to be expected for the benzene/pyridine system.

In passing, it should be mentioned that the equilibrium parameters are attainable from an analysis of the hyperfine splittings, using the relationship:

\[
\sigma_o = p_A^a_A + p_B^a_B
\]

(5-1)

for the fast exchange-averaged mean hyperfine splitting. Shklyaev and Anufrienko used this procedure to obtain equilibrium constants for CuDDC with pyridine in benzene. Eq. (5-1) was used here for the benzene/pyridine system, the results being the same as analysing the line position itself. Table 5-3 illustrates the data obtained. This method was not used for any other than the benzene/pyridine system, since by using the line positions directly exchange effects on both the isotropic and hyperfine values are implicitly included. The line position data, with appropriate units, are readily substituted into (4-4), (4-5) or (4-11) for further analysis.

It has been noted previously in this work that values of \( \omega_A \) obtained from extrapolation of the \( \langle \omega \rangle \) vs. \( L_0 \) plots to \( L_0 = 0 \) are consistently higher than those obtained in the cor-
<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>+3/2</th>
<th>+1/2</th>
<th>(K) (mole (\ell^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\omega_A^*)</td>
<td>(\omega_A^+)</td>
<td>(\omega_B^*)</td>
</tr>
<tr>
<td>280</td>
<td>59.612</td>
<td>59.483</td>
<td>59.133</td>
</tr>
<tr>
<td>285</td>
<td>59.607</td>
<td>59.478</td>
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</tr>
<tr>
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<td>59.601</td>
<td>59.474</td>
<td>59.156</td>
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<td>295</td>
<td>59.594</td>
<td>59.469</td>
<td>59.163</td>
</tr>
<tr>
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<td>59.587</td>
<td>59.465</td>
<td>59.156</td>
</tr>
<tr>
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<td>59.579</td>
<td>59.460</td>
<td>59.144</td>
</tr>
<tr>
<td>310</td>
<td>59.577</td>
<td>59.455</td>
<td>59.158</td>
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<td>315</td>
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<td>59.451</td>
<td>59.164</td>
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<td>59.559</td>
<td>59.446</td>
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<tr>
<td>325</td>
<td>59.554</td>
<td>59.441</td>
<td>59.145</td>
</tr>
</tbody>
</table>

* value obtained from least squares fit
+ value obtained from measurement in neat solvent
\(\$\) the value of \(K\) is the average between the values for the two hyperfine line studies; uncertainty \(\pm 0.02\).
### Parameters obtained from the line width data

**Line widths for the +3/2 line**

\((10^{-6} \text{ sec}^{-1})\)

<table>
<thead>
<tr>
<th>Temperature ((^\circ K))</th>
<th>(T^{-1}_{2A}^*)</th>
<th>(T^{-1}_{2A}^\dagger)</th>
<th>(T^{-1}_{2B}^*)</th>
<th>(T^{-1}_{2B}^\dagger)</th>
<th>(k_r^\dagger) ((x 10^{-8} \text{ sec}^{-1}))</th>
<th>(k_f^\dagger) ((=k_r^\dagger)) ((x 10^{-8} \text{ sec}^{-1} \cdot M^{-1}))</th>
<th>(\tau_B) ((10^9 \text{ sec}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>51.27</td>
<td>57.87</td>
<td>63.66</td>
<td>62.34</td>
<td>4.13</td>
<td>2.56</td>
<td>2.42</td>
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<tr>
<td>285</td>
<td>46.73</td>
<td>58.20</td>
<td>66.19</td>
<td>62.86</td>
<td>4.76</td>
<td>2.62</td>
<td>2.10</td>
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<tr>
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<td>64.99</td>
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<td>2.52</td>
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<td>54.43</td>
<td>67.31</td>
<td>5.55</td>
<td>2.36</td>
<td>1.80</td>
</tr>
<tr>
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<td>50.13</td>
<td>60.76</td>
<td>52.25</td>
<td>69.66</td>
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<td>2.17</td>
<td>1.71</td>
</tr>
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<td>51.86</td>
<td>62.00</td>
<td>50.58</td>
<td>71.98</td>
<td>6.25</td>
<td>2.13</td>
<td>1.60</td>
</tr>
<tr>
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<td>51.77</td>
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<td>6.62</td>
<td>1.99</td>
<td>1.51</td>
</tr>
<tr>
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<td>55.57</td>
<td>63.87</td>
<td>59.80</td>
<td>76.65</td>
<td>6.99</td>
<td>1.89</td>
<td>1.43</td>
</tr>
<tr>
<td>320</td>
<td>60.86</td>
<td>67.30</td>
<td>57.46</td>
<td>79.45</td>
<td>7.52</td>
<td>1.88</td>
<td>1.33</td>
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<tr>
<td>325</td>
<td>66.82</td>
<td>69.48</td>
<td>59.66</td>
<td>81.31</td>
<td>8.55</td>
<td>1.79</td>
<td>1.17</td>
</tr>
</tbody>
</table>

* * value obtained from the least squares fit

† value obtained from measurement in neat solvent


TABLE 5-3

Parameters obtained from a least squares fit of the hyperfine parameters

<table>
<thead>
<tr>
<th>Temperature (£K)</th>
<th>$A_A^*$</th>
<th>$A_A^+$</th>
<th>$A_B^*$</th>
<th>$A_B^+$</th>
<th>$\Delta A$ $(10^{-8} \text{sec}^{-1})$</th>
<th>$K$ $(\pm 0.02)$ (mole $\text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>14.333</td>
<td>13.441</td>
<td>11.063</td>
<td>11.424</td>
<td>3.274</td>
<td>0.62</td>
</tr>
<tr>
<td>285</td>
<td>14.283</td>
<td>13.409</td>
<td>11.081</td>
<td>11.531</td>
<td>3.202</td>
<td>0.60</td>
</tr>
<tr>
<td>290</td>
<td>14.247</td>
<td>13.378</td>
<td>11.063</td>
<td>11.486</td>
<td>3.184</td>
<td>0.51</td>
</tr>
<tr>
<td>295</td>
<td>14.211</td>
<td>13.348</td>
<td>11.207</td>
<td>11.675</td>
<td>3.004</td>
<td>0.47</td>
</tr>
<tr>
<td>300</td>
<td>14.175</td>
<td>13.315</td>
<td>11.189</td>
<td>11.612</td>
<td>2.986</td>
<td>0.33</td>
</tr>
<tr>
<td>305</td>
<td>14.121</td>
<td>13.283</td>
<td>11.099</td>
<td>11.666</td>
<td>3.022</td>
<td>0.34</td>
</tr>
<tr>
<td>310</td>
<td>14.081</td>
<td>13.252</td>
<td>11.153</td>
<td>11.819</td>
<td>2.932</td>
<td>0.30</td>
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<tr>
<td>315</td>
<td>14.040</td>
<td>13.222</td>
<td>11.243</td>
<td>11.837</td>
<td>2.806</td>
<td>0.30</td>
</tr>
<tr>
<td>320</td>
<td>13.995</td>
<td>13.189</td>
<td>11.207</td>
<td>11.837</td>
<td>2.788</td>
<td>0.26</td>
</tr>
<tr>
<td>325</td>
<td>13.959</td>
<td>13.157</td>
<td>11.225</td>
<td>11.891</td>
<td>2.734</td>
<td>0.24</td>
</tr>
</tbody>
</table>

* value obtained from least squares fit
† values obtained from measurements in neat solvent
responding neat solvents. In effect, this is precisely the least squares value of $\omega_A$, and as will be detailed later, in all solvents this "extrapolated" value of $\omega_A$ is the same for all solvents studied. Since it was expected that the difference between $\omega_A^{\dagger}$ (neat solvent) and $\omega_A^{*}$ (extrapolated or least squares result) should reflect some aspect of the solvation of CuDDC in benzene/pyridine mixtures, the benzene/pyridine system was examined at very low pyridine concentrations. The results are illustrated by fig. 5-4. Clearly, a significant decrease in $a_0$, from the trend illustrated by the solid line, occurs at base concentrations approaching that of the metal itself.

B. DETERMINATION OF STOICHIOMETRY: In chapter 3 a discussion of data presentation was outlined. In order to interpret the results of this thesis a knowledge of the adduct stoichiometry was required. The methods quoted in section A of this chapter, and shown to be entirely self-consistent, actually require the results of this section for confirmation.

Deranleau\textsuperscript{71} pointed out that a Scatchard\textsuperscript{80} plot of (3-15), represented as $\delta/[L_0]$ vs. $\delta$, must be linear over at least seventy-five percent of the saturation fraction before confirmation of the stoichiometric model yielding (3-15) can be made. Plots of the data obtained in these experiments, using the Scatchard presentation, are all linear over the entire $s$ range, which
Fig 5-4: Hyperfine splitting of CuDDC in benzene-pyridine solutions at low pyridine concentrations

\[ A_0 \text{ (GAUSS)} \]

Pyridine concentration (moles/litre)
covers the fraction $0.1 \leq s \leq 0.9$. Fig. (5-5) illustrates some of these plots. Benesi-Hildebrand\textsuperscript{81} plots ($\delta^{-1}$ vs. $[L_o]^{-1}$) for the same data are also linear, but the reliability of the plot is low because of the tendency of a reciprocal plot to crowd the data\textsuperscript{71}. This is ably illustrated in fig. (5-6), where the uncertainty problems are also shown. Because of the large uncertainties resulting from taking reciprocals of small numbers, the errors in low concentration data for this type of plot can become absurdly large.

The linearity of the plots confirms the 1:1 stoichiometry model used to derive (3-15). Hence the adduct formation process is describable in terms of:

\begin{equation}
(5-2) \quad \text{CuL}_2 + B \rightleftharpoons \text{CuL}_2 B
\end{equation}

Extrapolated values of $\omega_A$ were used to define $\delta$, since the neat solvent parameters are lower than the extrapolated ones.

Since $\delta = \omega - \omega_A$, values of $\delta$ calculated from $\omega_A^*$ will always have the same negative sign, since $\omega_A^* \geq \omega$. Values of $\omega_A^+$, however, will start out positive and change to negative as $\omega$ decreases with concentration. Clearly such a situation is unsatisfactory. An important point, in this regard, is that if neat solvent parameters are used for $\omega_A$, and $\omega$ is not measured down to very low base concentrations, then the difference between $\omega_A^*$ and $\omega_A^+$ may not be noticed. Under these conditions,
Fig 5-5: Scatchard plots of CuDDC with pyridine in solvents indicated.

- Triangles indicate toluene solution at 280°C.
- Circles indicate benzene solution at 300°C.
- Squares indicate chloroform solution at 320°C.
Fig 5-6: Benesi-Hildebrand plots for 3/2 Line
(pyridine in various solvents)
the value of $K$ calculated from (3-15), or equivalent expressions, will be higher from using $\omega_A^+$ than would be obtained by using $\omega_A^*$, since $\omega_A - \omega_B$, is then smaller.

The question arises: what would be the effect on a Scatchard plot of the experimental results if there were several competing equilibria involved rather than the single 1:1 process discussed so far? Although the results obtained confirm the 1:1 binding situation, consideration of the possibility of formation of 1:2 adducts, in addition, presents some interesting information. The situation to be considered is that discussed in chapter 3:

$$
K_1
$$

(5-3)

$$
CuL_2 + B \rightleftharpoons CuL_2B
$$

$$
CuL_2B + B \rightleftharpoons CuL_2B_2
$$

It is assumed to be extremely unlikely that only 2:1 adduct species could be formed, and this situation will not be considered explicitly. Using (3-23) values of $\langle \omega \rangle$ were calculated, assuming reasonable values of $\omega_A$, $\omega_B$, $\omega_C$, $K_1$ and $K_2$, over a wide base concentration range. Fast exchange conditions were assumed throughout. The results are illustrated in figs. (5-7) to (5-10). Fig. (5-7) shows that there is no possibility of $K_2 > K_1$ in this work; the Scatchard plot being extremely curved in this case. The other plots demonstrate that for two competing equilibria, no matter what the values
TABLE 5-4: SAMPLE DATA USED TO CONSTRUCT SCATCHARD MULTIPLE EQUILIBRIA PLOTS; FIGURE 5-7 AS AN EXAMPLE.*

Example 1: $\omega_A = 59.587 \text{ sec}^{-1}$; $\omega_B = 59.405 \text{ sec}^{-1}$; $\omega_C = 59.223 \text{ sec}^{-1}$

<table>
<thead>
<tr>
<th>[L] moles/1</th>
<th>AVERAGE FREQUENCY $x 10^{-9} \text{ sec}^{-1}$</th>
<th>$\delta x 10^{-9} \text{ sec}^{-1}$</th>
<th>$\delta/\l x 10^{-9} \text{ sec}^{-1} \text{ M}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>59.521</td>
<td>-0.066</td>
<td>-0.132</td>
</tr>
<tr>
<td>1.00</td>
<td>59.468</td>
<td>-0.119</td>
<td>-0.119</td>
</tr>
<tr>
<td>2.00</td>
<td>59.397</td>
<td>-0.190</td>
<td>-0.095</td>
</tr>
<tr>
<td>3.00</td>
<td>59.355</td>
<td>-0.032</td>
<td>-0.077</td>
</tr>
<tr>
<td>5.00</td>
<td>59.311</td>
<td>-0.276</td>
<td>-0.055</td>
</tr>
<tr>
<td>7.00</td>
<td>59.288</td>
<td>-0.299</td>
<td>-0.043</td>
</tr>
<tr>
<td>9.00</td>
<td>59.274</td>
<td>-0.313</td>
<td>-0.035</td>
</tr>
<tr>
<td>12.00</td>
<td>59.262</td>
<td>-0.325</td>
<td>-0.027</td>
</tr>
</tbody>
</table>

Example 2: $\omega_A = 59.587$ $\omega_B = 59.405$ $\omega_C = 59.223$ 

$K_1 = 0.10$ $K_2 = 0.38$

<table>
<thead>
<tr>
<th>[L] moles/1</th>
<th>AVERAGE FREQUENCY $x 10^{-9} \text{ sec}^{-1}$</th>
<th>$\delta x 10^{-9} \text{ sec}^{-1}$</th>
<th>$\delta/\l x 10^{-9} \text{ sec}^{-1} \text{ M}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-0.024</td>
</tr>
<tr>
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<td>-0.028</td>
</tr>
<tr>
<td>2.00</td>
<td>59.519</td>
<td>-0.068</td>
<td>-0.034</td>
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<td>59.478</td>
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<td>-0.036</td>
</tr>
<tr>
<td>5.00</td>
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<td>7.00</td>
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</tr>
<tr>
<td>9.00</td>
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<td>-0.029</td>
</tr>
<tr>
<td>12.00</td>
<td>59.299</td>
<td>-0.288</td>
<td>-0.024</td>
</tr>
</tbody>
</table>

* Terminology used is that in eq. 3-23.
Fig 5-7: Scatchard Plots of Benzene/Pyridine
Multiple Equilibria at 300 K
($K_1/K_2$ in parentheses)

$\omega_a = 5.9587 \times 10^4 (\text{sec}^{-1})$
$\omega_b = 5.9405$
$\omega_c = 5.9223$

$\delta / (L) \times 10^9 (\text{sec}^{-1} \text{M}^{-1})$

$\delta \times 10^{-3} (\text{sec}^{-1})$
Fig 5-8: Scatchard Plots of Benzene/Pyridine
Multiple Equilibria at 300 K
($K_1/K_2$ in parentheses)

$\omega_A = 59.587 \times 10^9 \text{sec}^{-1}$

$\omega_B = 59.223$

$\omega_C = 59.041$
Fig 5-9: Scatchard Plots of Benzene/Pyridine Multiple Equilibria at 300 K ($K_1/K_2$ in parentheses)

$\omega_a = 59.587 \times 10^9 \text{ sec}^{-1}$

$\omega_b = 59.223 \quad \omega_c = 58.859$
Fig 5-10: Scatchard Plots of Benzene/Pyridine Multiple Equilibria at 300 K

(K1/K2 in parentheses)

ω1 = 53.537 \times 10^9 \text{ sec}^{-1}

ω2 = 52.223

ω3 = 51.495
of \( \omega_B \) and \( \omega_C \), the plot of \( \delta/[L_0] \) vs. \( \delta \) is curved until \( K_1 >> K_2 \). Also, it is clear that a linear Scatchard plot can be obtained where \( K_1 > K_2 \), for the data plotted in the figures. The slopes of the linear Scatchard plots where \( K_2 \neq 0 \) are, however, quite different from the 1:1 (\( K_2 = 0 \)) cases. Thus values of \( K \) are different. The least squares values of \( K \) agree with the 1:1 plots, not the multiple equilibria cases, and hence 1:2 complex formation is unlikely.

Even without the epr evidence, the amount of 1:2 adduct formed would be very small, and depends on the formation constant \( \beta = K_1 K_2 \), which will be \( \sim 0.03 \) for CuDDC in benzene/pyridine at 300\(^\circ\)K. There will not be enough 1:2 adduct to render the 1:1 assumption inconsistent. Further, the fact that even at quite low temperatures no more than two epr spectra were observed indicates that only 1:1 adduct formation should be considered. Since the 2-picoline results in this thesis indicate that formation constants as low as \( \sim 0.02 \) can be measured, thus one would expect to observe any 1:2 adducts that might be formed, since it is expected that the hexa-coordinated complex would have noticeably different magnetic properties to penta-coordinated ones.

Consideration of previous work on copper(II) complexes \(^{108}\) indicates that 1:2 adducts of square planar copper(II) compounds are formed rarely; only when the parent complex is it-
self unstable. Also, the formation process illustrated by (5-3) would be expected to be a fast equilibrium followed by a slow 1:2 formation step, which would be easily detectable by epr methods. Stereochemical arguments have been invoked to show that in solution the addition of a sixth ligand to square planar complexes with a $d^9$ central ion is extremely unfavourable$^{110-113}$.

Thus the results of stereochemical and chemical arguments are identical to the conclusions drawn from consideration of Scatchard plots of the epr data, as might be expected, and confirm that CuDDC forms 1:1 adducts with weak neutral organic bases in inert solvents.

C. **SOLVENT EFFECTS:** The reaction of CuDDC with pyridine was studied in several solvents in order to compare solvent effects. The solvents used were benzene, toluene, and chloroform.

The equilibrium and rate constants were determined by the various methods outlined in chapters 3, 4 and 9. Tables 5-5 to 5-8 contain a summary of these results. Table 5-8, for instance shows the marked linewidth and $\omega_A - \omega_B$ temperature dependence. Table 5-5 contains similar information to that in Tables 5-1 to 5-3, but is repeated in the same form as Tables 5-6 and 5-7 for ease of comparisons. The results for the benzene/pyridine system were initially analysed at $5^\circ K$ intervals in order to ensure the accuracy and consistency of the methods of analysis used. Results for other solvents have been analysed at $10^\circ K$
TABLE 5-5
Parameters obtained from least squares fit of line position & linewidth for Benzene
(+3/2 line data only)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$A_0^*$ (G)</th>
<th>$A_1^+$ (G)</th>
<th>$\omega_A \times 10^9$ (sec)</th>
<th>$\omega_B \times 10^9$ (sec)</th>
<th>$\omega_C \times 10^9$ (sec)</th>
<th>$\omega_D \times 10^9$ (sec)</th>
<th>$k$ (a/mole)</th>
<th>$\tau_B \times 10^9$ (sec)</th>
<th>$k_r \times 10^{-8}$ (sec$^{-1}$)</th>
<th>$k_f = k_r \times 10^{-8}$ (sec$^{-1}$mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>280</td>
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<td>-74.72</td>
<td>59.612</td>
<td>59.483</td>
<td>59.133</td>
<td>59.196</td>
<td>0.60</td>
<td>2.42</td>
<td>4.13</td>
<td>2.56</td>
</tr>
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<td>59.601</td>
<td>59.474</td>
<td>59.156</td>
<td>59.205</td>
<td>0.53</td>
<td>1.91</td>
<td>5.24</td>
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<tr>
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<td>-78.74</td>
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<td>59.587</td>
<td>59.465</td>
<td>59.156</td>
<td>59.223</td>
<td>0.38</td>
<td>1.71</td>
<td>5.85</td>
<td>2.17</td>
</tr>
<tr>
<td>310</td>
<td>-78.28</td>
<td>-73.67</td>
<td>59.577</td>
<td>59.455</td>
<td>59.158</td>
<td>59.252</td>
<td>0.30</td>
<td>1.51</td>
<td>6.62</td>
<td>1.99</td>
</tr>
<tr>
<td>320</td>
<td>-77.80</td>
<td>-73.32</td>
<td>59.559</td>
<td>59.446</td>
<td>59.150</td>
<td>59.258</td>
<td>0.24</td>
<td>1.33</td>
<td>7.52</td>
<td>1.88</td>
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<tr>
<td>330</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* least squares value

† value from measurement in neat solvent

$ the K value has an uncertainty of ± 0.02. Uncertainties in $k_f$ are ± 0.12 x 10$^8$. Uncertainties in $\tau_B$ are ± 0.25 x 10$^{-9}$. 
TABLE 5.6
Parameters obtained from least squares fit of line position and linewidth in Toluene
(*3/2 line data only)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$A_0^{-}$ (G)</th>
<th>$A_0^{+}$ (G)</th>
<th>$\omega_A^{-} \times 10^{-9}$ (sec)</th>
<th>$\omega_A^{+} \times 10^{-9}$ (sec)</th>
<th>$\omega_B^{-} \times 10^{-9}$ (sec)</th>
<th>$\omega_B^{+} \times 10^{-9}$ (sec)</th>
<th>$K$ (sec$^{-1}$)</th>
<th>$\tau_B \times 10^{9}$ (sec)</th>
<th>$k_f \times 10^{-8}$ (sec$^{-1}$)</th>
<th>$k_f = K \times k \times 10^{-8}$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>-80.70</td>
<td>-75.32</td>
<td>59.639</td>
<td>59.498</td>
<td>59.137</td>
<td>59.174</td>
<td>0.92</td>
<td>4.60</td>
<td>2.17</td>
<td>1.99</td>
</tr>
<tr>
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<td>59.489</td>
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<tr>
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<td>-79.14</td>
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<td>59.478</td>
<td>59.144</td>
<td>59.205</td>
<td>0.47</td>
<td>2.40</td>
<td>4.18</td>
<td>1.96</td>
</tr>
<tr>
<td>300</td>
<td>-78.65</td>
<td>-74.30</td>
<td>59.578</td>
<td>59.472</td>
<td>59.144</td>
<td>59.223</td>
<td>0.36</td>
<td>1.97</td>
<td>5.08</td>
<td>1.83</td>
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<tr>
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<td>-78.20</td>
<td>-73.96</td>
<td>59.568</td>
<td>59.463</td>
<td>59.144</td>
<td>59.252</td>
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<td>6.06</td>
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<td>-73.64</td>
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<td>59.455</td>
<td>59.144</td>
<td>59.258</td>
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<td>1.35</td>
<td>7.41</td>
<td>1.63</td>
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<td>-73.28</td>
<td>59.556</td>
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<td>0.18</td>
<td>1.04</td>
<td>9.61</td>
<td>1.73</td>
</tr>
</tbody>
</table>

* value from least squares fit
† value from measurement in neat solvent
$ the K value has an uncertainty of ±0.02. Uncertainty in $k$ is ±0.12 x 10$^8$,
uncertainty in $\tau_B$ is ±0.25 x 10$^{-9}$.
<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$A_0^*$ (G)</th>
<th>$A_0^+$ (G)</th>
<th>$\omega_A^+\times10^{-9}$ (sec$^{-1}$)</th>
<th>$\omega_A^+\times10^{-9}$ (sec$^{-1}$)</th>
<th>$\omega_B^+\times10^{-9}$ (sec$^{-1}$)</th>
<th>$\omega_B^+\times10^{-9}$ (sec$^{-1}$)</th>
<th>$k^$ (sec$^{-1}$)</th>
<th>$k_B^\times10^{-9}$ (sec$^{-1}$)</th>
<th>$k_f^*k_B^\times10^{-8}$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-75.68</td>
<td>59.654</td>
<td>59.100</td>
<td>59.174</td>
<td>59.100</td>
<td>0.60</td>
<td>5.10</td>
<td>1.96</td>
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<td>-75.51</td>
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<td>59.091</td>
<td>59.196</td>
<td>59.091</td>
<td>0.41</td>
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<td>-75.10</td>
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<td>59.079</td>
<td>59.205</td>
<td>59.079</td>
<td>0.30</td>
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<td>4.15</td>
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<td>-74.70</td>
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<td>59.084</td>
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<td>59.084</td>
<td>0.24</td>
<td>1.66</td>
<td>6.02</td>
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<td>59.104</td>
<td>0.15</td>
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<tr>
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<td>-73.46</td>
<td>59.549</td>
<td>59.090</td>
<td>59.268</td>
<td>59.090</td>
<td>0.12</td>
<td>0.80</td>
<td>12.50</td>
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</table>

* value from least squares fit
+ value from measurement in neat solvent

$\$ uncertainty in $K \pm 0.02$. Uncertainty in $k$ is $\pm 0.12 \times 10^8$, uncertainty in $\tau_B$ is $\pm 0.25 \times 10^{-9}$. 
**TABLE 5-8**

Frequency difference and line width data (+3/2 line) only for benzene, toluene and chloroform

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>BENZENE</th>
<th>TOLUENE</th>
<th>CHLOROFORM</th>
<th>PYRIDINE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\omega_A - \omega_B$</td>
<td>$T_{12}^{-1}$</td>
<td>$T_{12}^{-1}$</td>
<td>$T_{12}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>(10^{-6} sec^{-1})</td>
<td>(10^{-6} sec^{-1})</td>
<td>(10^{-6} sec^{-1})</td>
<td>(10^{-6} sec^{-1})</td>
</tr>
<tr>
<td>270</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5024</td>
</tr>
<tr>
<td>280</td>
<td>0.4793</td>
<td>51.27</td>
<td>57.87</td>
<td>0.4652</td>
</tr>
<tr>
<td>290</td>
<td>0.4443</td>
<td>46.76</td>
<td>58.81</td>
<td>0.4477</td>
</tr>
<tr>
<td>300</td>
<td>0.4312</td>
<td>50.13</td>
<td>60.76</td>
<td>0.4344</td>
</tr>
<tr>
<td>310</td>
<td>0.4190</td>
<td>51.77</td>
<td>63.56</td>
<td>0.4236</td>
</tr>
<tr>
<td>320</td>
<td>0.4094</td>
<td>60.86</td>
<td>67.30</td>
<td>0.4169</td>
</tr>
<tr>
<td>330</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.4134</td>
</tr>
</tbody>
</table>

* least squares fitted values

† values measured in neat solvents
intervals. Further, the temperature range over which the investigations were carried out was limited by the boiling and freezing points of the solvents, and by the necessity to confine the experiments to the fast exchange region. Hence the temperature range considered was 0°C to 60°C, usually.

From the temperature dependence of the equilibrium and rate constants, it is possible to estimate the thermodynamic parameters characterising the adduct formation process in the various solvents. This was accomplished by using the van't Hoff/Arrhenius law (see Appendix 1 for derivation and use of the relationship), obtaining \( E \), the energy of activation for the process being considered, from a plot of \( \ln K \) (or \( \ln k \)) vs. \( 1/T \). These values are summarised in Table 5-9, along with some values from other work.

In figs. 5-11 and 5-12 are shown the Arrhenius plots for equilibrium and rate constants, respectively, for the three solvents. The plots indicate that the results can be confidently interpreted in terms of a simple Arrhenius law. All thermodynamic parameters were calculated for \( T = 300^\circ K \) for ease of comparison with the results of other workers.

As can be seen in Table 5-9, negative activation energies are obtained for benzene and toluene solvent systems for the adduct formation process. This will be discussed in more detail later, but it is useful to note here that these negative values were found reproducible and consistent, and are
Fig 5-11: Arrhenius plots for equilibrium constants for solvents indicated. Squares indicate chloroform, circles indicate benzene, triangles indicate toluene.
Fig 5-12: Arrhenius plots for rate constants for solvents indicated.

- $k_r$ indicated by open symbols
- $k_f$ indicated by closed symbols
- circles indicate benzene
- triangles indicate toluene
- squares indicate chloroform
# Table 5-9: Thermodynamic Data

(Several Cu(II) complexes with pyridine in various solvents)

<table>
<thead>
<tr>
<th>Complex*</th>
<th>Solvent</th>
<th>Temp</th>
<th>K</th>
<th>ΔH°</th>
<th>ΔS°</th>
<th>Kₚ</th>
<th>ΔHₚ</th>
<th>ΔSₚ</th>
<th>ΔHᵣ</th>
<th>ΔSᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(ON-BCD)₂</td>
<td>CH₃C₆H₇</td>
<td>298</td>
<td>0.40</td>
<td>-5.0</td>
<td>-19</td>
<td>20</td>
<td>-</td>
<td>-0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Cu(DDC)₂</td>
<td>CH₃C₆H₅</td>
<td>298</td>
<td>0.49</td>
<td>-4.9</td>
<td>-18.3</td>
<td>5.60</td>
<td>2.17</td>
<td>-2.9</td>
<td>-30</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu(ODC)₂</td>
<td>C₆H₆</td>
<td>300</td>
<td>0.38</td>
<td>-4.9</td>
<td>-18.3</td>
<td>5.60</td>
<td>2.17</td>
<td>-2.9</td>
<td>-30</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu(ODC)₂</td>
<td>C₆H₆</td>
<td>300</td>
<td>0.76</td>
<td>-5.4</td>
<td>-20.0</td>
<td>5.08</td>
<td>1.83</td>
<td>-1.0</td>
<td>-24</td>
<td>4.3</td>
</tr>
<tr>
<td>Cu(ODC)₂</td>
<td>CHCl₃</td>
<td>300</td>
<td>0.24</td>
<td>-5.2</td>
<td>-20.1</td>
<td>6.02</td>
<td>1.42</td>
<td>0.5</td>
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<td>5.7</td>
</tr>
<tr>
<td>Cu(t-BuOAc)₂</td>
<td>C₆H₁₂</td>
<td>298</td>
<td>37.7</td>
<td>-7.1</td>
<td>-16.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu(Acac)₂</td>
<td>C₆H₆</td>
<td>303</td>
<td>4.7</td>
<td>-6.5</td>
<td>-18.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu(3-Metacac)₂</td>
<td>C₆H₆</td>
<td>303</td>
<td>2.0</td>
<td>-3.0</td>
<td>-8.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Abbreviations:

Cu(ON-BCD)₂ - Copper (II) bis (di-n-butylidithiocarbamate)
Cu(DDC)₂ - Copper (II) bis (diethyldithiocarbamate)
Cu(t-BuOAc)₂ - Copper (II) bis (t-butylacetacetae)
Cu(3-Metacac)₂ - Copper (II) bis (3-methylacetylacetonate)

(a) ref. 86  
(b) ref. 109  
(c) this work  
(d) ref. 132  
(e) ref. 112
not the result of experimental error or an artifact of the methods used. Up until now, negative activation energies in solution have been reported only for radical recombination reactions.

Other results obtained will be introduced and discussed as they are needed, in order to facilitate certain aspects of the discussion.

D. **EFFECTS OF VARIATION OF BASE:** It was considered important not only to study solvent effects on the equilibrium:

\[
(5-4) \quad \text{CuDDC} + \text{base} \rightleftharpoons \text{CuDDC-base}
\]

but also to investigate the effect of variation of the base. In principle, any Lewis base maintaining the equilibrium in (5-4) is suitable, as long as the forward and reverse rates of reaction are fast by epr standards. That is, of course, if the results are to be interpreted within this approximation, as is the case in this work. Relatively small changes in base strength, and hence formation constant, were found to have quite pronounced effects upon the exchange. A quite narrow range of rates is available for study by the fast exchange approximation; perhaps \(10^8\) to \(10^9\) sec\(^{-1}\) for the systems studied in this work. Thus it was found that pyridine and a series of methyl-substituted pyridines were the most suitable bases to use. Piperidine, for instance, is a strong enough base that many of the spectra ob-
tained near room temperature were still in the slow or intermediate regions of exchange. Fig. 5-13 illustrates the temperature variation of a piperidine/toluene system. The bases chosen for study were 2-, 3-, and 4-picoline (2-, 3-, and 4-methyl pyridine), and 3,4- and 2,6-lutidine (3,4- and 2,6-dimethyl pyridine). These are all commercially available in high purity.

All least squares analysis results, as for the solvents, are most conveniently summarised in tabular form, and are presented in Tables 5-10 to 5-13, along with derived equilibrium and rate constants. The data for pyridine have already been given in Tables 5-1, 5-2, 5-3, and 5-5. Probably because of steric effects caused by the two methyl groups the data for 2,6-lutidine indicate that no adduct formation occurred with this base. In effect, it behaves as an inert solvent. The experimental data are presented in Table 5-14, and fig. 5-14 illustrates the variation of frequency with base strength for several temperatures. This trend can be seen to be markedly different from that obtained with other bases, as illustrated by fig. 5-2. It was found difficult to dissolve CuDDC in 2,6-lutidine, dissolution being effected after warming to 40°C for 1 - 2 hours. It was also noticeably more difficult to dissolve CuDDC in 2-picoline than in other pyridines (2,6-lutidine excepted). These facts are reflected in the results, shown in Table 5-10. No equilibrium or rate data could be obtained at
Fig 5-13: Temperature Dependence of CuDDC in Toluene-Piperidine Solutions

261 K

3200 G

279 K

291 K

299 K
TABLE 5-10

Parameters obtained from least squares fit of line position and linewidth for 2-picoline in benzene

(+3/2 line data only)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>A_o B</th>
<th>ω_A x 10^{-9}</th>
<th>ω_A x 10^{-9}</th>
<th>ω_B x 10^{-9}</th>
<th>ω_B x 10^{-9}</th>
<th>K$</th>
<th>τ_B x 10^9</th>
<th>k_r x 10^{-8}</th>
<th>k_f = k_k x 10^{-7}</th>
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<tbody>
<tr>
<td>275</td>
<td>-71.25</td>
<td>59.569</td>
<td>59.576</td>
<td>59.394</td>
<td>59.176</td>
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<td>0.054</td>
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<tr>
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<td>59.548</td>
<td>59.553</td>
<td>59.439</td>
<td>59.222</td>
<td>0.050</td>
<td>1.07</td>
<td>9.35</td>
<td>4.68</td>
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<td>59.512</td>
<td>59.462</td>
<td>59.214</td>
<td>0.023</td>
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</tr>
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</table>

$+0.05$

† measured in neat solvent (B refers to 2-picoline, A to benzene)

* obtained from least squares fit

$ maximum errors in K are $0.02$ (from Scatchard plot reproducibility). Uncertainty in $k \sim 0.02 x 10^8$
in $\tau_B \sim 0.25 x 10^{-9}$. 
TABLE 5-11
Parameters obtained from least squares fit of line position and line width for 3-picoline in benzene

(+3/2 line only)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$a_o^{B+}$ (G)</th>
<th>$\omega_A^* x 10^{-9}$ (sec$^{-1}$)</th>
<th>$\omega_B^* x 10^{-9}$ (sec$^{-1}$)</th>
<th>$\omega_B^+ x 10^{-9}$ (sec$^{-1}$)</th>
<th>$(\omega_A^* - \omega_B^*) x 10^{-9}$</th>
<th>$k^S$ (1/mole)</th>
<th>$\tau_B x 10^9$</th>
<th>$k_R x 10^{-8}$</th>
<th>$k_f = Kk_R x 10^{-8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>-61.60</td>
<td>59.604</td>
<td>59.109</td>
<td>59.145</td>
<td>0.495</td>
<td>1.10</td>
<td>3.64</td>
<td>2.75</td>
<td>3.02</td>
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<td>0.79</td>
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<td>3.08</td>
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<td>59.549</td>
<td>59.143</td>
<td>59.195</td>
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<td>0.57</td>
<td>2.47</td>
<td>4.05</td>
<td>2.33</td>
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<td>300</td>
<td>-63.90</td>
<td>59.540</td>
<td>59.147</td>
<td>59.206</td>
<td>0.394</td>
<td>0.49</td>
<td>2.20</td>
<td>4.55</td>
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<tr>
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<td>-64.75</td>
<td>59.528</td>
<td>59.154</td>
<td>59.228</td>
<td>0.374</td>
<td>0.37</td>
<td>1.79</td>
<td>5.60</td>
<td>2.05</td>
</tr>
<tr>
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<td>59.518</td>
<td>59.162</td>
<td>59.247</td>
<td>0.357</td>
<td>0.29</td>
<td>1.50</td>
<td>6.67</td>
<td>1.96</td>
</tr>
<tr>
<td>335</td>
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<td>59.508</td>
<td>59.166</td>
<td>59.270</td>
<td>0.342</td>
<td>0.20</td>
<td>1.32</td>
<td>7.58</td>
<td>1.52</td>
</tr>
</tbody>
</table>

+0.05

$^+$ measured in neat solvent. B refers to 3-picoline, A to benzene

* obtained from least squares fit

$^S$ uncertainty in $K = \pm 0.02$, in $k = \pm 0.20 \times 10^8$, in $\tau_B, \pm 0.25 \times 10^{-9}$. 
### TABLE 5-12

Parameters obtained from least squares fit of line position and linewidth data for 4-picoline in benzene

(+3/2 line only)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>( a_0^B )</th>
<th>( \omega_A \times 10^{-9} )</th>
<th>( \omega_B \times 10^{-9} )</th>
<th>( \omega_A^+ \times 10^{-9} )</th>
<th>( (\omega_A - \omega_B) \times 10^{-9} )</th>
<th>( k^S )</th>
<th>( \tau_B \times 10^9 )</th>
<th>( k_r \times 10^{-8} )</th>
<th>( k_f = k_k \times 10^{-8} )</th>
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</thead>
<tbody>
<tr>
<td>275</td>
<td>-61.11</td>
<td>59.613</td>
<td>59.098</td>
<td>59.134</td>
<td>0.515</td>
<td>1.47</td>
<td>5.58</td>
<td>1.79</td>
<td>2.63</td>
</tr>
<tr>
<td>285</td>
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<td>59.576</td>
<td>59.113</td>
<td>59.148</td>
<td>0.463</td>
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<td>4.42</td>
<td>2.26</td>
<td>2.38</td>
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<td>59.547</td>
<td>59.122</td>
<td>59.164</td>
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<td>3.00</td>
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<td>59.585</td>
<td>59.124</td>
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<td>3.28</td>
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</tr>
<tr>
<td>310</td>
<td>-63.25</td>
<td>59.518</td>
<td>59.128</td>
<td>59.190</td>
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<td>0.46</td>
<td>2.42</td>
<td>4.13</td>
<td>1.88</td>
</tr>
<tr>
<td>320</td>
<td>-63.96</td>
<td>59.505</td>
<td>59.131</td>
<td>59.208</td>
<td>0.373</td>
<td>0.34</td>
<td>1.87</td>
<td>5.35</td>
<td>1.83</td>
</tr>
<tr>
<td>330</td>
<td>-64.71</td>
<td>59.496</td>
<td>59.135</td>
<td>59.227</td>
<td>0.360</td>
<td>0.27</td>
<td>1.48</td>
<td>6.76</td>
<td>1.81</td>
</tr>
<tr>
<td>+0.05</td>
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<td></td>
</tr>
</tbody>
</table>

\( ^\dagger \) measured in neat solvent. B refers to 4-picoline, A to benzene

\* obtained from least squares fit

\$ uncertainty in \( K \sim 0.02 \), in \( k \sim 0.20 \times 10^8 \), in \( \tau_B \sim 0.25 \times 10^{-9} \).
Parameters obtained from least squares fit of line position and line width data for 3,4-lutidine in benzene

(*3/2 line only)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$a^B_0$ (G)</th>
<th>$\omega_A^* \times 10^{-9}$</th>
<th>$\omega_B^* \times 10^{-9}$</th>
<th>$\omega_B^+ \times 10^{-9}$</th>
<th>$(\omega_A^* - \omega_B^+)^* \times 10^{-9}$</th>
<th>$K^$</th>
<th>$\tau_B \times 10^9$</th>
<th>$k_r \times 10^{-8}$</th>
<th>$k_f = Kk \times 10^{-8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>-59.48</td>
<td>59.698</td>
<td>59.066</td>
<td>59.088</td>
<td>0.632</td>
<td>2.02</td>
<td>5.78</td>
<td>1.73</td>
<td>3.49</td>
</tr>
<tr>
<td>285</td>
<td>-60.90</td>
<td>59.636</td>
<td>59.105</td>
<td>59.126</td>
<td>0.531</td>
<td>1.55</td>
<td>4.93</td>
<td>2.03</td>
<td>3.15</td>
</tr>
<tr>
<td>295</td>
<td>-62.20</td>
<td>59.589</td>
<td>59.134</td>
<td>59.160</td>
<td>0.455</td>
<td>1.14</td>
<td>4.25</td>
<td>2.35</td>
<td>2.67</td>
</tr>
<tr>
<td>300</td>
<td>-62.82</td>
<td>59.571</td>
<td>59.145</td>
<td>59.177</td>
<td>0.426</td>
<td>0.97</td>
<td>4.04</td>
<td>2.48</td>
<td>2.41</td>
</tr>
<tr>
<td>310</td>
<td>-64.00</td>
<td>59.545</td>
<td>59.164</td>
<td>59.208</td>
<td>0.381</td>
<td>0.71</td>
<td>3.32</td>
<td>3.01</td>
<td>2.12</td>
</tr>
<tr>
<td>320</td>
<td>-65.00</td>
<td>59.528</td>
<td>59.184</td>
<td>59.234</td>
<td>0.344</td>
<td>0.56</td>
<td>3.00</td>
<td>3.33</td>
<td>1.87</td>
</tr>
<tr>
<td>335</td>
<td>-66.40'</td>
<td>59.515</td>
<td>59.188</td>
<td>59.270</td>
<td>0.327</td>
<td>0.38</td>
<td>2.62</td>
<td>3.82</td>
<td>1.45</td>
</tr>
</tbody>
</table>

+0.05

† measured in neat solvent. B refers to 3,4-lutidine, A to benzene

* obtained from least squares fit

$^\$ uncertainty in K $\sim 0.02$, in $k_\sim 0.20 \times 10^8$, in $\tau_B \sim 0.25 \times 10^{-9}$
### TABLE 5-14

Representative data obtained for 2,6-lutidine in benzene

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$a_o^{B+}$ (G)</th>
<th>$g_o^{B+}$</th>
<th>$\omega_A \times 10^{-9}$ (sec$^{-1}$)</th>
<th>$\omega_B \times 10^{-9}$ (sec$^{-1}$)</th>
<th>$(\omega_A - \omega_B) \times 10^{-9}$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>-78.72</td>
<td>2.04186</td>
<td>59.580</td>
<td>59.585</td>
<td>-0.005</td>
</tr>
<tr>
<td>285</td>
<td>-78.35</td>
<td>2.04201</td>
<td>59.567</td>
<td>59.575</td>
<td>-0.006</td>
</tr>
<tr>
<td>295</td>
<td>-77.93</td>
<td>2.04215</td>
<td>59.560</td>
<td>59.564</td>
<td>-0.004</td>
</tr>
<tr>
<td>300</td>
<td>-77.72</td>
<td>2.04223</td>
<td>59.556</td>
<td>59.559</td>
<td>-0.003</td>
</tr>
<tr>
<td>310</td>
<td>-77.30</td>
<td>2.04237</td>
<td>59.546</td>
<td>59.548</td>
<td>-0.003</td>
</tr>
<tr>
<td>320</td>
<td>-76.88</td>
<td>2.04258</td>
<td>59.536</td>
<td>59.537</td>
<td>-0.001</td>
</tr>
<tr>
<td>335</td>
<td>-76.25</td>
<td>2.04273</td>
<td>59.523</td>
<td>59.521</td>
<td>+0.002</td>
</tr>
</tbody>
</table>

† measured in neat solvent. A refers to benzene, B to 2,6-lutidine.
Fig 5-14: Line Position vs Concentration for 2,6-lutidine in benzene.
all for 2,6-lutidine, and 2-picoline yielded very small equilibrium constants, the smallest not being obtainable from the least squares analysis of the epr data, but from the Scatchard plots of the data. Fig. 5-15 illustrates these results. It was also found impossible to correlate the linewidths with any reasonable trend above 310°C, for 2-picoline, presumably because K was so small. Results from Arrhenius plots for this case are limited to the range 270-310°C.

Thermodynamic results, obtained from Arrhenius plots, are illustrated in figs. 5-16, 5-17, and 5-18, and summarised in Table 5-15. The pertinent base strengths are also given in 5-15. It may be noted that, again, a series of negative activation energies for the forward process in (5-4) is obtained.
Fig 5-15: Scatchard Plots for 2-picoline in Benzene
<table>
<thead>
<tr>
<th>BASE</th>
<th>pKa</th>
<th>K</th>
<th>(k_r \times 10^8)</th>
<th>(k_p \times 10^8)</th>
<th>(\Delta H^\circ)</th>
<th>(\Delta S^\circ)</th>
<th>(\Delta H_f^\dagger)</th>
<th>(\Delta S_f^\dagger)</th>
<th>(\Delta H_r^\dagger)</th>
<th>(\Delta S_r^\dagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYRIDINE</td>
<td>5.22</td>
<td>0.38</td>
<td>2.17</td>
<td>5.80</td>
<td>-5.01</td>
<td>-18.3</td>
<td>-2.85</td>
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<td>-11.6</td>
</tr>
<tr>
<td>2-PICOLINE</td>
<td>5.96</td>
<td>0.05</td>
<td>0.47</td>
<td>9.35</td>
<td>-3.13</td>
<td>-16.6</td>
<td>+5.30</td>
<td>-5.8</td>
<td>+8.43</td>
<td>+10.6</td>
</tr>
<tr>
<td>3-PICOLINE</td>
<td>5.63</td>
<td>0.49</td>
<td>2.21</td>
<td>4.55</td>
<td>-5.18</td>
<td>-18.7</td>
<td>-2.42</td>
<td>-28.5</td>
<td>+2.75</td>
<td>-9.8</td>
</tr>
<tr>
<td>4-PICOLINE</td>
<td>5.98</td>
<td>0.62</td>
<td>2.04</td>
<td>3.28</td>
<td>-5.65</td>
<td>-19.8</td>
<td>-1.90</td>
<td>-26.9</td>
<td>+3.76</td>
<td>-7.1</td>
</tr>
<tr>
<td>3,4-LUTIDINE</td>
<td>6.46</td>
<td>0.97</td>
<td>2.41</td>
<td>2.48</td>
<td>-5.17</td>
<td>-17.3</td>
<td>-3.29</td>
<td>-31.1</td>
<td>+1.90</td>
<td>-13.8</td>
</tr>
</tbody>
</table>

† Uncertainties in \(\Delta H^\circ\)=±0.2 kcals/mole, in \(\Delta S^\circ\)=±1.2 e.v.; values for these parameters derived from temperature dependence of equilibrium constant.
Fig 5-16: Arrhenius plots of equilibrium constants for various pyridines.
Fig 5-17: Arrhenius Plots for Several Pyridines (forward rates)
Fig 518: Arrhenius Plots for Several Pyridines (reverse rates)
CHAPTER 6

SOLVENT AND TEMPERATURE EFFECTS ON EPR SPECTRA, AND A COMPARISON WITH OTHER WORK

A. SOLVENT EFFECTS ON EPR PARAMETERS: The effects on copper(II) epr parameters of varying the solvent have been studied quite extensively for copper(II) bis(acetylacetonate) and various substituted derivatives. No previous work on solvent effects has been published for CuDDC, however. The results obtained in this work show a definite solvent (and temperature) dependence of the isotropic hyperfine splitting and g value. Table 6-1 summarises these results.

Now it may be remembered that in chapter 5 mention was made of the fact that extrapolated values of $\omega_A$, $\omega_A^*$, were consistently higher than those measured in neat solvent, $\omega_A^\dagger$. It may also be noted that for all three solvents, benzene, toluene, and
<table>
<thead>
<tr>
<th>TEMPERATURE (°K)</th>
<th>270</th>
<th>280</th>
<th>290</th>
<th>300</th>
<th>310</th>
<th>320</th>
<th>330</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
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<td>-74.37</td>
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<td>-73.67</td>
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<td>2.04544</td>
<td>2.04545</td>
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<td>-73.64</td>
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<td>2.04666</td>
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<td>2.04213</td>
<td>2.04224</td>
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<td>-77.80</td>
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<td>2.04206</td>
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<td>-63.65</td>
<td>-64.55</td>
<td>-65.15</td>
<td>-65.78</td>
<td>-66.50</td>
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<td>2.05622</td>
<td>2.05514</td>
<td>2.05435</td>
<td>2.05360</td>
<td>2.05295</td>
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<td>-55.92</td>
<td>-56.60</td>
<td>-57.22</td>
<td>-57.80</td>
<td>-58.30</td>
</tr>
<tr>
<td></td>
<td>2.05977</td>
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<td>2.05860</td>
<td>2.05823</td>
<td>2.05800</td>
<td>2.05750</td>
<td>2.05690</td>
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</table>

* Quoted are ($^\circ$) values, $g_0$ in Gauss.
chloroform, the $\omega_A^*$ values are equal within experimental error. The extrapolated values (least squares fitting of the results defines $\omega_A$ as that value obtained by extrapolating the $\omega$ vs. $L_0$ curve to $L_0 = 0$) can evidently be associated with a "pure-solvent" situation.

The equivalence of the extrapolated values on all solvents at all temperatures is illustrated in Tables 5-5 to 5-7. Considering the values of the hyperfine splitting associated with the extrapolated value of $\omega_A^*$, $a_A^*$, it is clear from Table 6-1 that only measurements made in neat cyclohexane and carbon tetrachloride approach $a_A^*$, which averages to $-78.70 \pm 0.15$ G at 300°K. In all other solvents, the values of $a_0$ are lower than this value.

It was found difficult to dissolve CuDDC in both cyclohexane and carbon tetrachloride, a fact that suggests that these two solvents can be regarded as quite inert or non-coordinating. It may also be noted that the value of $a_0$ for 2,6-lutidine at 300°K was $-77.70$ G, and great difficulty in dissolving CuDDC in this solvent has already been reported in this thesis (or see chapter 9). The presence of methyl groups adjacent to the nitrogen nucleus evidently prevents interaction between 2,6-lutidine and copper(II), hence the non-coordinating nature of this solvent, which behaves much like cyclohexane and carbon tetrachloride with respect to CuDDC. Further, the known co-ordinating solvents, piperidine and the pyridines, all have values of $a_0$ that increase (become less negative) as the base strength in-
creases. Table 6-2 gives the base strengths and $a_o$ values at 300°C:

<table>
<thead>
<tr>
<th>Base</th>
<th>$pK_a$</th>
<th>$a_o$ (G)</th>
<th>Dipole Moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>5.22</td>
<td>-64.5</td>
<td>2.33</td>
</tr>
<tr>
<td>2-Picoline</td>
<td>5.96</td>
<td>-73.0</td>
<td>1.93</td>
</tr>
<tr>
<td>3-Picoline</td>
<td>5.63</td>
<td>-63.9</td>
<td>2.54</td>
</tr>
<tr>
<td>4-Picoline</td>
<td>5.98</td>
<td>-62.6</td>
<td>2.75</td>
</tr>
<tr>
<td>3,4-Lutidine</td>
<td>6.46</td>
<td>-62.8</td>
<td>1.87</td>
</tr>
<tr>
<td>2,6-Lutidine</td>
<td>6.72</td>
<td>-77.7</td>
<td>1.66</td>
</tr>
<tr>
<td>Piperidine</td>
<td>11.28</td>
<td>-56.7</td>
<td>1.29</td>
</tr>
</tbody>
</table>

There is clearly a correlation between decreasing co-ordinating ability of the base, taking into account steric hindrance, and more negative, or increasing values of $a_o$. There is apparently no significant correlation with dipole moment unless only the picolines are considered. Thus it seems that the extrapolated values of $a_A$ and $\omega_A$ can be regarded as solvent-interaction-free parameters, and hence define a level of inertness. The deviation of most solvents from this inert value indicates a small degree of co-ordination by the solvent. Adding very small amounts of pyridine then must disturb this co-ordination.
in some manner that does not lead to co-ordination of the pyridine, but a simple clustering of molecules of solvent and base about the copper(II) nucleus. This would be an inert or non-coordinating situation, and hence the value of $\omega_A$, or $a_A$, increases to that expected from smooth extrapolation of $\omega$ vs. $L_0$ to low $L_0$. Then as more pyridine is added the magnitude of $a_0$ decreases with increasing pyridine concentration as coordination occurs. The remarkable consistency, at all temperatures investigated, of the fitted values of $\omega_A$ for the three solvents is rather strong evidence that these values do indeed represent an inert solvent, since there are noticeable differences in the values of $\omega_A$ obtained in the neat solvents. A general trend of $a_0$ suggests a decreasing level of inertness in the order (300°K):

(6-1) \[ \text{CCl}_4 > \text{C}_6\text{H}_6 > \text{CHCl}_3 > \text{CH}_3\text{C}_6\text{H}_5 > \text{C}_6\text{H}_5 > \text{C}_5\text{H}_2\text{N} > \text{C}_5\text{H}_{11}\text{N} \]

This seems intuitively reasonable, apart from details about benzene and toluene, perhaps, and agrees with the findings of Selbin\textsuperscript{134} on the donor properties of various solvents.

The conclusions of Antosik et al\textsuperscript{133} , confirmed by Adato and Eliezer\textsuperscript{131} for copper(II) acetylacetonate, is that as solvent interactions along the axial direction increase, the g value will increase and the $a_0$ value decrease (if $a_0 < 0$, magnitude of $a_0$ decreases). Kuska and Rogers\textsuperscript{141} earlier concluded similarly for the interaction of copper(II) acetylacetonates with basic solvents. The trends, in fact, are predicted to hold for
both $a_0$ and $A$.

An unusual exception to the trends noted above is given in the work of Libutti et al., who investigated the variation of the epr parameters for copper(II) t-butylacetoacetate with various solvents. They found that $a_0$ increased, relative to cyclohexane (-70.0 G), for the series: carbon tetrachloride (-71.3 G), benzene (-72.4 G), and chloroform (-74.8 G). This trend is opposite to that obtained here, and that expected, and Libutti et al. interpreted it as evidence that $a_0$ values increase (become less negative) as inertness increased. It is not likely that copper t-butylacetoacetate solvates differently from copper acetylacetone and CuDDC, but that is the only conclusion available from comparison of the results of this work, and others, with that of Libutti et al.

B. ULTRA-VIOLET AND VISIBLE SPECTRA: Libutti et al. supported their epr findings by noting a shift in the visible region for copper t-butylacetoacetate in cyclohexane, compared to chloroform. Thus UV and visible spectra were examined in this work in several solvents and pyridines to determine whether or not the epr parameters are sensitive to coordination effects. One would expect shifts in the UV and visible spectra upon co-ordination, the magnitude of the shift perhaps reflecting something of the degree of co-ordination. Vanngard and Pettersson measured such shifts for various divalent coinage metal dialkyldithiocarbam-
ates, with results agreeing essentially with those obtained here. Table 6-3 illustrates these findings:

TABLE 6-3: UV/VISIBLE MAXIMA FOR CuDDC IN VARIOUS SOLVENTS AT 298°K

<table>
<thead>
<tr>
<th>solvent</th>
<th>visible $\lambda_{\text{max}}$ (cm$^{-1}$)</th>
<th>UV $\lambda_{\text{max}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>23,030</td>
<td>34,020</td>
</tr>
<tr>
<td>benzene</td>
<td>22,980</td>
<td>34,145</td>
</tr>
<tr>
<td>chloroform</td>
<td>22,940</td>
<td>34,350</td>
</tr>
<tr>
<td>pyridine</td>
<td>21,740</td>
<td>33,100</td>
</tr>
<tr>
<td>2,6-lutidine</td>
<td>22,960</td>
<td>33,175</td>
</tr>
</tbody>
</table>

The shifts here are smaller than those obtained by Vänn-gård and Pettersson, but the trend is the same. The combination of epr and UV/visible absorption results indicate that more coordination does take place between CuDDC and benzene, and chloroform, than in cyclohexane, and the pyridine results substantiate this. The UV results for 2,6-lutidine and pyridine appear to be somewhat out of place, in comparison to epr and visible spectra results, probably because of other electronic effects associated with these bases.

C. TEMPERATURE EFFECTS: Table 6-1 indicates that the isotrop-
ic epr parameters of CuDDC in solution are highly temperature
dependent. Temperature dependence of the hyperfine splittings
of copper(II) complexes in solution has been noted before, and
these authors ascribed the dependence to a vibrational ef-
fect wherein the motion of the copper atom and its nearest neigh-
bours is described in terms of Boltzmann distributions:

\[ \frac{a_i}{a_0} = \frac{a_0 + \sum a_i \exp(-\Delta E_i/kT)}{1 + \sum \exp(-\Delta E_i/kT)} \]

where \( a_0 \) is the hyperfine splitting in the vibrational ground
state, \( a_i \) that in the \( i \)'th vibrational state, and \( \Delta E_i \) the ener-
gy difference between the ground and \( i \)'th vibrational levels.

Eq. (6-2) has been reasonably successful in interpreting temper-
ature dependences for proton hyperfine splittings in simple
organic free radicals, where only one excited vibrational
state is considered in the calculation. Luckhurst and Falle obtained reasonable agreement with the experimentally-observed
trend using (6-2) in the same fashion, but pointed out that it
is unreasonable, with the amount of data presently available,
to attempt to interpret the right hand side of (6-2) with res-
pect to epr parameters. No attempt will be made here to give
a quantitative interpretation of the temperature dependence,
but it has been reported that a decrease of \( |a_0| \) with
increasing temperature points to an increase of covalent bond-
ing as the temperature is increased. Non-coordinating solvents
do behave in this fashion, 2,6-lutidine included, in this work. The trends for co-ordinating solvents are exactly opposite to this, leading to the suggestion that covalency decreases with increasing temperature for a co-ordinating solvent. Thus it is unlikely that a simple covalency argument is sufficiently general to explain these opposite trends with temperature, and that the explanation lies in a combination of vibrational and covalency effects.

An important ramification of the temperature dependence of hyperfine parameters is that the commonly used assumption:

\[(6-3) \quad a_0 = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz})\]

is valid only at the temperature at which all parameters are measured. In other words, it is commonplace in epr studies for measurements of \(a_0\) to be made in solution, and either \(A_\parallel\) (= \(A_{zz}\), for an axial case) or \(A_\perp\) (= \(A_{xx} = A_{yy}\)) to be measured in frozen solution. The other parameter, \(A_\perp\) or \(A_\parallel\), is often difficult to measure and is estimated from \(a_0\) and \(A_\parallel\) or \(A_\perp\) using (6-3); for example:

\[(6-4) \quad A_\perp = (3a_0 - A_\parallel)/2\]

\(A_\perp\) measured in this fashion will certainly be subject to error.

D. COMPARISONS WITH OTHER WORK: Although it may seem out of place at this point, a comparison with the only other work pub-
lished on CuDDC interacting with Lewis bases in inert solvents is useful here because of the close connection with the temperature dependence of epr parameters just mentioned.

Very recently, Corden and Rieger\textsuperscript{86} and Shklyaev and Anufrienko\textsuperscript{109}, published studies on fast exchange equilibria involving Lewis acid-base adduct formation, with copper(II) dialkyl-dithiocarbamates as the Lewis acid. Corden and Rieger\textsuperscript{86} studied the system copper(II) bis(di-n-butylidithiocarbamate) with pyridine, piperidine, and n-hexylamine in methylcyclohexane, analysing the results in a fashion similar to that employed here. A direct comparison of these results is not possible, although the thermodynamic parameters for pyridine (see Table 5-9) seem reasonable. The lifetimes, however, are quite different to those obtained here. Close examination of their work reveals several quite important inconsistencies. For the study with pyridine, these authors found it necessary to both (i) constrain $\omega_A - \omega_B$ to be temperature independent, and (ii) to use the piperidine value of $\omega_A - \omega_B$, since they found it impossible to obtain consistent values of $k_r$ otherwise. It may be noted further that the concentration range covered (0 - 2.5 M) is insufficient to obtain reliable results for $K$ and $k$ (see discussion in chapters 3 and 5), and that only three temperatures were measured. The limited amount of data taken thus renders the pyridine results subject to uncertainty.

Constraining $\omega_A - \omega_B$ to be temperature independent will
introduce large errors\(^{116}\), and means that values of \(\tau_B\) will be
too high when \(\omega_A - \omega_B\) is less than the "temperature-independent"
value, and too low when otherwise. This, in turn, will lead to
errors in \(\Delta H^\#\). Increasing the value of \(\omega_A - \omega_B\) to that for
piperidine (for CuDDC this represents a 30% increase) will simi-
larly lead to smaller values of \(\tau_B\) than should be the case.
Both these constraints are arbitrary and not difficult to avoid,
as demonstrated in this work, and lead to serious limitations
upon the conclusions that may be inferred by Corden and Rieger.

The more recent study by Shklyaev and Anufrienko\(^{109}\) in-
volved reaction between CuDDC and pyridine in toluene. Values
of \(K\) obtained are in good agreement with those obtained here,
but discrepancies exist in the evaluations of \(\Delta H^\#\). Once again,
these authors make the assumption that \(a_o\) and \(g_o\), and the neat
solvent parameters, are temperature independent. Tables of
data given by these authors indicate that this is not so, as
stressed here earlier, and to make use of this assumption
invites large errors\(^{116}\). Examination of their data (not all
the necessary data is provided so exact reconstruction of
their results is not possible) shows that \(\omega_A - \omega_B\) should change
by 30% over the temperature range they consider. Appropriate
corrections to \(\tau_B\) and hence \(k_T\) then indicate that \(\Delta H^\#\) should
be \(\sim 5\) kcals/mole, rather than the value 8.6 kcals/mole ob-
tained. This would be in agreement with that obtained here,
and would yield a similar value of \(\Delta H^\#\) to that quoted in this
work. The method used by Shklyaev and Anufrienko is that of Dye and Dalton, which is based on determining the \( m_I \)-dependent coefficients of the linewidths (eqs. (4-6) and (4-7)), and which is equivalent to that used here, with one caution.

To extract the linewidth coefficients from only a four line epr spectrum, as is the case with copper(II) complexes in solution, is a difficult task at low or moderately low temperatures \((T < 280^\circ K)\). At these temperatures the two low field lines become quite broad, often broad enough to overlap. Linewidth measurements on such lines are subject to large errors, and extraction of \( m_I \)-dependent coefficients is likely to be subject to equally large uncertainty. Fig. 6-1 illustrates typical CuDDC broadening. The vanadyl eight-line spectrum is not subject to such uncertainties, for instance, since it is relatively easy to least-squares analyse the linewidths observed for the parameters \( \alpha, \beta, \gamma, \) and \( \delta \).

A final point with respect to the study of Shklyaev and Anufrienko is that the equilibrium constants were measured over a wide pyridine concentration range, but rate constants were evaluated only at 0.475 M pyridine in toluene. This may not cause any increase in error in the results, but it is clear that this region is not the most sensitive to the effects of exchange. The maximum exchange effects occur at pyridine concentrations \( \geq 1 \) M for the temperature range 0 - 60°C, and it would be expected that in order to minimise any possible errors,
Fig 6-1: Typical Temperature Effects on CuDDC in 4-Picoline, as an example.
measurements of the exchange rate should be made over a reasona-
able concentration range, including very carefully the region of
maximum exchange. Regions not in a sensitive part of the con-
centration range will be relatively insensitive to small changes
in $\tau_B$. These qualitative considerations, coupled with those of
Deranleau, suggest that all rate processes should
be studied not only over a reasonable range of temperature, but
also over a range of concentration sufficient to include all ef-
fects of exchange. It is also unnecessary, as well as unwise,
to assume that epr parameters are temperature independent in or-
der to evaluate rate and equilibrium data. When such assump-
tions are made, it is impossible to treat the results in strict-
est confidence. Since insufficient fast exchange data are availa-
able for study, the rejection of some data as unreliable is un-
fortunate.
CHAPTER 7

DISCUSSION OF RESULTS

A. SOME THOUGHTS ON THE INTERPRETATION OF EQUILIBRIUM AND RATE DATA.

a) Introductory Remarks: The results quoted in chapter 5 demonstrated that the various pyridine adducts with CuDDC in the solvents studied are of 1:1 stoichiometry. The mechanism leading to the observed rate constants, and hence thermodynamics, will be discussed as a function of solvent. These considerations will be shown to be consistent with the results obtained in benzene with various pyridines.

Table 5-9, repeated here as Table 7-1, shows that the process:

$$
(7-1) \quad \text{CuDDC} + B \xrightarrow{k_f} \xleftarrow{k_r} \text{CuDDC}\cdot B
$$
<table>
<thead>
<tr>
<th>System</th>
<th>$pK_a^{H_2O}$</th>
<th>Dipole Moment (D)</th>
<th>K (1/mole)</th>
<th>$\Delta H^o$ (kcal/mole)</th>
<th>$\Delta S^o$ (e.u)</th>
<th>$\Delta G^o$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene/Pyridine</td>
<td>5.22</td>
<td>2.33</td>
<td>0.38</td>
<td>-4.9</td>
<td>-18.4</td>
<td>+0.5</td>
</tr>
<tr>
<td>Toluene/Pyridine</td>
<td>5.22</td>
<td>2.33</td>
<td>0.36</td>
<td>-5.4</td>
<td>-19.7</td>
<td>+0.6</td>
</tr>
<tr>
<td>Chloroform/Pyridine</td>
<td>5.22</td>
<td>2.33</td>
<td>0.24</td>
<td>-5.2</td>
<td>-20.1</td>
<td>+0.8</td>
</tr>
<tr>
<td>Benzene/2-picoline</td>
<td>5.96</td>
<td>1.93</td>
<td>0.05</td>
<td>-3.7</td>
<td>-16.4</td>
<td>+1.7</td>
</tr>
<tr>
<td>Benzene/3-picoline</td>
<td>5.63</td>
<td>2.54</td>
<td>0.49</td>
<td>-5.2</td>
<td>-18.7</td>
<td>+0.4</td>
</tr>
<tr>
<td>Benzene/4-picoline</td>
<td>5.98</td>
<td>2.75</td>
<td>0.62</td>
<td>-5.7</td>
<td>-19.8</td>
<td>+0.3</td>
</tr>
<tr>
<td>Benzene/3,4-lutidine</td>
<td>6.46</td>
<td>1.87</td>
<td>0.97</td>
<td>-5.2</td>
<td>-17.4</td>
<td>+0.0</td>
</tr>
</tbody>
</table>
where B is a suitable base and \( K = \frac{k_c}{k_r} \), is highly solvent dependent. That is, examination of rate constants and thermodynamic parameters reveals a solvent dependence of some sort. It was established that the values of \( \tau_B \), and hence \( k_r \), were not themselves concentration dependent. Some studies of the effects of solvent on equilibrium constants of adducts formed from a Lewis acid-base reaction of square planar copper(II) complexes with organic bases have been reported\(^{112,114,132}\), but theoretical and/or experimental studies of the rates and mechanisms of fast equilibria involving neutral species are nonexistent. It may be noted also that the concept of equilibrium is difficult to discuss for processes with low or negative energies of activation\(^{153}\).

b) Interpretation of Equilibrium Constants: Table 7-1 shows the variation of equilibrium constant with solvent. Immediately obvious is that the formation (equilibrium) constants are uniformly much smaller for CuDDC than for copper(II) bis(\( \beta \)-diketonates). This is presumably because the \( \beta \)-diketonate complexes are less stable than CuDDC in inert solvents, and this suggests that CuDDC is a much weaker Lewis acid than the \( \beta \)-diketonate complexes.

As already noted, few studies have been reported on solvent effects on equilibrium constants for Lewis acid-base equilibria involving square planar copper(II) complexes in non-coordinating solvents\(^{112,114,132,145}\). Many have been carried out in benzene\(^{146-148}\). The results here, and elsewhere\(^{132}\), suggest that
benzene is not a good example of an inert solvent, as often supposed, and may interact considerably with the ligand or chelate structure of the metal complex.

Previous work has established\textsuperscript{112,132} that for copper(II) \(\beta\)-diketonates the adduct formation constants decrease in the order: benzene > toluene > chloroform. The results here, at all temperatures from 270 - 330°K, agree with this order. Heats of solvation have been measured for pyridine in various solvents\textsuperscript{132}, and these are as follows: benzene = -0.01 kcal/mole, chloroform = -1.82 kcals/mole, cyclohexane = +1.84 kcals/mole, and carbon tetrachloride = +0.17 kcal/mole. These results suggest a strong interaction between pyridine and chloroform, presumably via hydrogen bonding. It is known, for instance\textsuperscript{149}, that pyridine and carbon tetrachloride form weak adducts. The near zero heat of solvation of pyridine in benzene reflects the similar structure of these two solvents. Thus the lower heat of formation for CuDDC and pyridine in chloroform, compared to benzene, reflects the fact that the heat evolved in solution of pyridine in chloroform would have to be at least partially restored in the process of adduct formation\textsuperscript{112}, thus leading to lower formation constants.

This statement is actually an empirical assessment of a more detailed consideration of the formation process to be discussed shortly. The similarity of formation constants for benzene and toluene simply reflects the lack of differentiation by pyridine between the two similar structures. The temperature dependence
of $K$ in both solvents points out, however, that only near room temperature is the similarity as strong as just quoted. At lower temperatures toluene becomes progressively more ordered (epr measurements at X-band become impossible at $-30^\circ C$ due to absorption of microwave energy by toluene. Dielectric relaxation measurements show a maximum at this temperature for X-band frequencies. Hence the implication is that toluene becomes an ordered array of oriented dipoles) raising the temperature tends to destroy this, and the values for $K$ become as much as 50% larger than for benzene.

It is also evident that the overall enthalpies and entropies of formation are reasonably similar, leading one to suspect that changing the solvent does not have a dramatic effect on the overall process. The value of $\Delta H^o$, $\sim -5$ kcals/mole, is within the range, $-2 < \Delta H^o < -10$ kcals/mole, thought to typify formation of a Cu-N bond$^{114}$. This value can be compared to that suggested for the Cu-0 bond in bis(2,4-pentanedione)-copper(II) of 48.7 kcals/mole$^{150}$. The Cu-N bond formed is hence relatively weak.

Table 7-1 also contains the data for several bases in benzene solution. The variation of formation constant can be summarised for all temperatures studied as decreasing in the order:

$$3,4\text{-}lutidine > 4\text{-}picoline > 3\text{-}picoline > \text{pyridine}$$

$$\text{pyridine} >> 2\text{-}picoline$$
2,6-Lutidine presumably formed an even weaker bond than 2-picoline, to the extent that it was not measurable. The base strengths quoted in Table 6-1 are in the same order as the $K$ values, except for the sterically-hindered 2-picoline and 2,6-lutidine. The same trends with variation of base have been noted by other workers studying copper(II) bis($\beta$-diketonates)$^{86}$. Also, Graddon and Hsu$^{148}$ obtained a low value of $K$, about half that for 2-picoline, for 2,4,6-collidine. Thus steric effects are quite pronounced for substituents at the 2- or both 2- and 6- positions of pyridine, presuming similar solvent interactions, for nucleophilicity towards copper(II). That the base strengths in aqueous solution do not reflect this hindrance is due simply to the small size of the proton. Changing the reference acid to progressively larger species leads to a regular change in the observed order of base strengths in the series: pyridine, 2-picoline, and 2,6-lutidine$^{179}$. Obviously 2,6-lutidine fails to form a bond, in any measurable sense, to copper(II), but 2-picoline can presumably approach the bonding site in a configuration suitable for some bond formation. This bond formation would be expected to require more solute-base encounters for 2-picoline than for an unhindered pyridine. Hence the overall enthalpy of formation is considerably lower for 2-picoline.

The trend in overall enthalpy of formation is:

$$(7-3) \quad 4\text{-picoline} > 3,4\text{-lutidine} > 3\text{-picoline} > \text{pyridine}$$
pyridine >> 2-picoline

and that for entropy of formation is:

4-picoline > 3-picoline > pyridine > 3,4-lutidine
3,4-lutidine > 2-picoline

The trends are the same as formation constant and base strength (neglecting 2-picoline) except for the anomalous position of 3,4-lutidine. It has been noted that in aqueous solution the enthalpy and entropy of ionization for 2,6-lutidine are lower than expected$^{166,178}$, considering the trend observed in the picolines. Ionisation effects are not important here, but the lower values of $\Delta H^\circ$ and $\Delta S^\circ$ may reflect an inability to form a bond at every encounter with the metal, due to repulsion and hindrance effects caused by adjacent methyl groups, but that once a favourable encounter has occurred, a strong Cu-N bond results, hence the higher value of $K$ (and lower value of $k_r$).

c) **Interpretation of rate constants:** Solvent variation of the rates, as well as base variation, is shown in Table 7-2. For the three solvents, benzene, toluene, and chloroform, a decrease in forward rate over the series is noted; there is an especially noticeable decrease in chloroform. In contrast, the rates for the various bases in pyridine are reasonably consistent, except for 2-picoline. Walker et al$^{20}$ obtained a sim-
# TABLE 7-2

**Kinetic Data for all Systems (300°K)**

<table>
<thead>
<tr>
<th>System</th>
<th>$pK_{a}^{H_{2}O}$</th>
<th>Dipole Moment</th>
<th>$k_f \times 10^{-8}$</th>
<th>$k_r \times 10^{-8}$</th>
<th>$\Delta H_f^\ne$</th>
<th>$\Delta S_f^\ne$</th>
<th>$\Delta H_r^\ne$</th>
<th>$\Delta S_r^\ne$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene/pyridine</td>
<td>5.22</td>
<td>2.33</td>
<td>2.17</td>
<td>5.8</td>
<td>-2.9</td>
<td>-30.0</td>
<td>2.1</td>
<td>-11.6</td>
</tr>
<tr>
<td>Toluene/pyridine</td>
<td>5.22</td>
<td>2.33</td>
<td>1.83</td>
<td>5.08</td>
<td>-1.0</td>
<td>-24.1</td>
<td>4.3</td>
<td>-4.4</td>
</tr>
<tr>
<td>Chloroform/pyridine</td>
<td>5.22</td>
<td>2.33</td>
<td>1.45</td>
<td>6.02</td>
<td>0.5</td>
<td>-19.5</td>
<td>5.7</td>
<td>+0.6</td>
</tr>
<tr>
<td>Benzene/2-picoline</td>
<td>5.96</td>
<td>1.93</td>
<td>0.47</td>
<td>9.35</td>
<td>+5.3</td>
<td>-5.8</td>
<td>8.4</td>
<td>+10.6</td>
</tr>
<tr>
<td>Benzene/3-picoline</td>
<td>5.63</td>
<td>2.54</td>
<td>2.21</td>
<td>4.55</td>
<td>-2.4</td>
<td>-28.5</td>
<td>2.7</td>
<td>-9.8</td>
</tr>
<tr>
<td>Benzene/4-picoline</td>
<td>5.98</td>
<td>2.75</td>
<td>2.04</td>
<td>3.28</td>
<td>-1.9</td>
<td>-26.9</td>
<td>3.8</td>
<td>-7.1</td>
</tr>
<tr>
<td>Benzene/3,4-lutidine</td>
<td>6.46</td>
<td>1.87</td>
<td>2.41</td>
<td>2.48</td>
<td>-3.3</td>
<td>-31.1</td>
<td>1.9</td>
<td>-13.8</td>
</tr>
</tbody>
</table>
ilar forward rate at $300^\circ K$ to that obtained here, for the reaction of vanadyl acetylacetonate with 2-picoline. Noting that for bases other than 2-picoline the forward rates are not ligand base-strength-dependent in benzene, one might summarise the findings by asserting that the forward rate process is not ligand dependent, but is solvent dependent. Reverse rates, however, are very much ligand dependent, whereas solvent dependence remains the same. Such conclusions, at $300^\circ K$, might appear to be sound. However, to interpret such relationships amongst rates in terms of some specific mechanism can be dangerous. That this is so can be shown after consideration of the temperature variation of the rate constants.

As with the equilibrium constants, the temperature dependence of the rate constants can be related to enthalpies and entropies of reaction by the Arrhenius/van't Hoff relationship discussed in Appendix 1. These parameters are tabulated in Table 7-2. The overall negative entropy changes reflect the simple disorder argument that two molecules are forming one complex, and thus losing some disorder. The negative entropy of formation in each case is relatively large, as expected. The negative entropies of dissociation, however, presumably reflect the fact that there must be solvent participation and steric effects involved also in the formation/dissociation process. Clearly the dissociation of the complex is highly favoured for 2-picoline, compared to the other bases. On the other hand,
chloroform, known to react quite strongly with pyridine, has a lower $\Delta S^\circ_T$ than the other solvents. The negative values of $\Delta S^\circ_T$, apart from solvent and steric effects, do not follow directly the order-disorder argument, although the $\Delta S^\circ_T$ values are markedly decreased in the reverse direction. Possibly the remaining contribution is from the fact that many copper(II) square planar complexes, and CuDDC in particular, in solution prefer to be four-coordinate.

A close look at the entropies and enthalpies of reaction reveals a compensation, or isokinetic, effect$^{164}$. In other words, a plot of $\Delta H^\circ$ vs. $\Delta S^\circ$ will be linear with slope $T^\circ$, the isokinetic temperature. This temperature is that for which the rates are equal. The isokinetic plots are shown in figures 7-1 and 7-2 for the solvents and bases, respectively. Such a correlation relates an isoequilibrium set of reactions to an isoequilibrium temperature, $\Delta H/\Delta S$, and a condition for the existence of the effect is a common mechanism$^{163}$. Steric interactions might cause restrictions of motion or reaction in the reacting molecules of some process and must be accounted for in any isokinetic plot. More detail about the isokinetic behaviour will be given later, but for now the important point to note is its existence in processes dominated by solvation changes, and having common mechanistic pathways$^{166,167}$.

As the name implies, an isokinetic plot means a temperature exists at which all rates are equal, for some formation or
A benzene
B toluene
C chloroform

Fig 7-1: Isokinetic plots for solvents
○ forwards △ reverse
Fig 7-2: Isokinetic plots for bases.

- 1 3,4-lutidine
- 2 pyridine
- 3 3-picoline
- 4 4-picoline
- 5 2-picoline

- Forwards
- Reverse
dissociation process. Clearly, on either side of this temperature the order of rate constants must exactly be reverse to the other. Hence, studies made at one temperature based on a series of ordered reaction rates are incomplete. The mechanism proposed for any isokinetic series of reactions must be able to justify this reversal. A recent theory of concerted solvent interaction in labile metal complex reactions proposed by Bennetto and Caldin takes such behaviour into account. The work of Rorabacher et al, however, is performed at room temperature only. Hence conclusions drawn from such results must be subject to the limitation that they are valid only on one side of the isokinetic temperature and hence remain somewhat incomplete. It is difficult to envisage, in fact, how solvent structure effects could be taken into account adequately through measurements made at only one temperature, in light of available information on isokinetic reactions, and the implications of the work of Bennetto and Caldin.

**d) Fast Reactions and Arrhenius/van't Hoff relationships:**
As a final point in this section, it might be useful to reiterate a few cautionary remarks about the use of Arrhenius plots for fast processes. For more details on the derivation of Arrhenius relationships, Appendix 1 and standard texts are available.

The Arrhenius activation energy, described by:

\[
k = A \exp(-E_A/RT)
\]
is usually interpreted as the difference between the average energy of the reacting complexes and the average energy of all the colliding pairs of reactant molecules present\textsuperscript{153}. Several distinct contributions make up this activation energy, usually considered to be bond energies, repulsion forces, electrostatic interactions and reorganisation of solvent molecules. This sort of interpretation of $E_A$ usually assumes that this value is temperature independent and can be associated with its value at absolute zero temperature. Hence no account of thermal energy is included. Linear Arrhenius plots, as obtained in this work, for reactions involving no change in ionic charge are justifiable evidence for the temperature independent approximation to $E_A$, however\textsuperscript{153}, and $E_A$ can be reasonably associated with the height of the potential energy barrier to the transition state. Success in its application tends to alleviate any fear of the potential errors involved.

Fast reactions clearly have a low energy of activation (hence a high collision or encounter rate), and are not always well described by transition state theory. Gas phase reactions, in particular, have been shown to not maintain an equilibrium distribution of energy for low energy barriers ($E/RT \ll 5$)\textsuperscript{153}. In solution, however, it is likely that solvent molecules will tend to maintain an equilibrium distribution, and not be subject to large deviations from transition state theory. Also, the small values of $K$ observed in this work indicate that products and reactants are depleted and replenished at fairly fast rates, and equi-
librium is maintained. The negative activation energies are not simply related to traditional ideas, and, in fact, staying within transition state theory means that at least a two step process must be involved, the first of which is reversible.\textsuperscript{117}

Thus the interpretation of the results will be kept within the bounds of transition state theory, but precise definition of the transition state will prove to be difficult. It would appear, however, that very fast reactions that are more than unimolecular, and reversible, must always be subject to similar limitations.

B. THE FORWARD, OR ASSOCIATIVE, REACTION:

a) Current Ideas, Rate Constants, and Thermodynamic Parameters: A brief description of the solvent effects on forward, or associative, rates has already been given. Several recent reviews have discussed fast metal-complex formation reactions.\textsuperscript{32,37,151,152} The accepted consensus that solvent or ligand exchange at a metal ion in solution often proceeds via a dissociative interchange mechanism incorporating a rapid pre-equilibrium invokes the formation of an outer-sphere complex, and may be illustrated as follows; for an octahedrally solvated metal ion,

\begin{equation}
\text{(7-5)} \quad \text{MS}^2_6 \ldots \ldots \text{L}^q^- \\
\end{equation}

where \text{L}^q^- is some incoming ligand species. The ligand does not have to be charged, necessarily. The overall process may be re-
where \( p \) represents the number of solvent molecules returned to the bulk solvent. Solvent exchange can be incorporated as a trivial extension, replacing ligand with solvent. This scheme was initially proposed by Eigen\textsuperscript{151}, along with several other mechanisms, to explain a series of experimental results involving metal ions. One important assumption is inherent. That is, that the solvation shell of the ligand is several orders of magnitude more labile than that of the metal\textsuperscript{37}. Such an assumption is reasonable for most ion pair and metal complex reactions, but fast Lewis acid-base reactions involving neutral molecules may not always be within such an assumption. It is known, for instance, that the high rate constants (\( > 10^7 \text{ sec}^{-1} \)) observed for the replacement of solvent by incoming ligand in some reactions\textsuperscript{151,153} mean that loss of solvent from the coordination sphere of the metal ion is very easy, and consequently ligand attack is the rate-determining step. As noted earlier with respect to equilibria and activation energies, very fast reactions are perhaps not entirely within the framework of conventional mechanisms.

Much evidence in favour of (7-6) is (i) that the observed forward rate constant is second order, first in metal and first in ligand, and (ii) that the rate of complex formation is usually simi-
lar to the rate of solvent exchange. There will be little or no ligand dependence (not concentration dependence, but dependence on the coordinating or attacking properties of the ligand) in such a mechanism \(^{156}\), in the sense that there is only partial involvement of the ligand, with outer sphere complexes as precursors \(^{152}\). Langford and Muir have shown \(^{154}\) the importance of this kind of mechanism for complex formation with inert ions such as cobalt(III).

A study of adduct formation between various amines and nickel(II) \(\beta\)-diketonates \(^{155,163}\) has also concluded that the important process in the formation is the nickel-amine bond breaking step, although when uncomplexed amine is present in large excess, then pseudo first order kinetics may be the true description, owing to preferential solvation of the adduct by the amine.

Consideration of a purely dissociative mechanism:

\[
\begin{align*}
\text{MS}^{2+}_m & \overset{k_{ab}}{\longrightarrow} \text{MS}^{2+}_{m-1} + \text{LS}_n & \overset{k_{cd}}{\longrightarrow} \text{MLS}^{2+}_{m+n-p-1} \\
\text{MS}^{2+}_m & \overset{k_{ba}}{\longrightarrow} \text{MS}^{2+}_{m-1} + \text{LS}_n & \overset{k_{dc}}{\longrightarrow} \text{MLS}^{2+}_{m+n-p-1}
\end{align*}
\]

involves an intermediate of reduced co-ordination number, and one would expect some dependence on ligand for the rates. This mechanism is expected to show larger rate constants the weaker the metal-solvent bond \(^{37}\), irrespective of the nature of a particular ligand. It has been argued that reaction through a reduced-coordinate intermediate is energetically unfavourable \(^{180}\), but it would appear that the purely dissociative mechanism may be favoured for strongly co-ordinating solvents \(^{161,181}\).

Solvent effects must be considered, therefore, as
part of the dissociative mechanisms, and both inner sphere and outer sphere effects need to be discussed. Rorabacher\textsuperscript{35,161} has proposed a model to explain certain solvent effects within the framework of the dissociative mechanism, based on studies made in mixed solvents\textsuperscript{161}. It is reasonable to assume that if a dissociative process is found for individual solvents, then the same mechanism should hold in mixtures of these solvents. With this in mind, Rorabacher proposed\textsuperscript{161} that a "pure solvent of strong co-ordinating nature results in a more stable five-coordinated metal ion transition state relative to its six-coordinated ground state than does a pure solvent of weaker co-ordinating ability", based on results obtained for Ni\textsuperscript{2+} in water, methanol, and ammonia solutions. This leads, when mixed solvents are considered, to the conclusion that substitution of weaker co-ordinating ligands in the inner solvation sphere decelerates the metal bond rupture rate for all other ligands in the inner sphere. In other words, the five co-ordinate transition state is destabilised relative to the hexa-coordinate ground state. Thus if no steric effects occur, as might with multidentate ligands, the reaction rate of a solvated metal ion should reflect the rupture rate of the weakest metal-solvent bond in the inner solvation, or coordination, complex. This rate can be modified quite markedly by the variation in donor strength of other ligands (solvents) in the complex. Solvent mixture results should then reflect the balance between weak and strong bonding species present in a particular metal.
inner sphere. These inner sphere considerations apply particularly well to ligand exchange in fairly strong solvents such as water or methanol, where a highly solvated metal ion is usually considered. By reducing the inner sphere effects (with a quinque-dentate ligand) at Ni(II) Rorabacher also managed to show that outer sphere effects are important in exchange processes. The similarity of this restricted inner sphere complex situation to the CuDDC case studied here is notable. Rorabacher's proposal was put forward to explain the fact that when inner complex effects are minimised, both formation and dissociation rates for ammonia exchange are increased as the methanolic content of the solvent is increased. This effect is opposite that for which the inner sphere effects were discussed, whereby as inner-coordinated solvent molecules changed from water to methanol the weaker metal-methanol bonds tended to lower the bond-breaking rate for metal-water bonds. For pure solvents, this leads to slower ammonia exchange rate in methanol than in water. Thus Rorabacher's outer sphere mechanism to explain the opposite effect was that methanol is more effective in "pulling" an ammonia molecule from the coordinating site than is water. The affinity of a particular leaving group for a particular solvent molecule is expected to be reflected as trends in dissociation rate constants as a function of solvent composition. Effects such as hydrogen bond formation would be expected to contribute.

It is clear, therefore, that the proposals put forward by
Rorabacher, which evidently consistently interpret ammonia exchange rates in various solvents with Ni(II) ions, may explain the results obtained here.

First, it is useful to note that a solvent pre-equilibrium process:

\[
\begin{align*}
(7-8) & \quad B + \text{Solvent} \rightleftharpoons B(\text{Solvent}) \\
& \quad \text{CuL}_2 + \text{Solvent} \rightleftharpoons \text{CuL}_2(\text{Solvent}) \\
& \quad \text{CuL}_2(\text{Solvent}) + B(\text{Solvent}) \rightleftharpoons (\text{CuL}_2 \cdot B)(\text{Solvent})
\end{align*}
\]

cannot explain the observed solvent trends in forward enthalpies. That this is so can be seen by considering that the overall enthalpy change may be expressed as:

\[
(7-9) \quad \Delta H^\circ = \Delta H_f^\circ - \Delta H_r^\circ + \Delta H_{\text{solv}}
\]

where \(\Delta H_{\text{solv}}\) represents some sort of contribution from the solvent pre-equilibrium. Rearranging, one obtains:

\[
(7-10) \quad \Delta H_f^\circ = \Delta H^\circ - \Delta H_{\text{solv}} + \Delta H_r^\circ
\]

Now \(\Delta H_{\text{solv}}\) for the solvent/ligand interaction is variable with varying solvent, and it may be assumed that a constant contribution is made by the solvation of the metal complex. So noting that \(\Delta H_{\text{solv}}\) for benzene/pyridine is \(\approx 0\) kcals/mole, and for chloroform/pyridine is \(-1.86\) kcals/mole\(^{132}\), it would appear that \(\Delta H_f^\circ\), from (7-10) does indeed increase on going from benzene...
to chloroform, as observed. However, this model cannot include
the changes in $\Delta H_f^\ddagger$, which are observed to increase from benzene
to chloroform, but which (7-10) predicts will decrease in the
same order using the values for $\Delta H_{solv}$ just quoted. Both trends
in $\Delta H_f^\ddagger$ and $\Delta H_I^\ddagger$ require information about the other, and hence
pre-equilibrium arguments can be used to qualitatively rationalise solvent trends, but cannot be very specific.

Rorabacher's results were obtained for $\sim 300^\circ$K, so it will
be fruitful to see whether or not his inner sphere and outer
sphere solvation models can definitely reproduce the trends ob-
served. As noted already the forward rates for CuDDC in various
solvents with pyridine decrease from benzene to chloroform, and
the enthalpies of formation increase over the same order. Schem-
atically this may be represented as:

\[
\text{CuDDC} \quad \text{CuDDC - benzene} \quad \text{CuDDC - toluene} \quad \text{CuDDC - chloroform}
\]

where the arrows represent the various $\Delta H_f^\ddagger$ to be expected. The
fact that $\Delta H_f^\ddagger$ is negative for benzene and toluene is not impor-
tant in the present discussion, so only the trends in rates will
be considered. In terms of Rorabacher's proposals for inner
sphere effects, then, one would expect the reduced-coordinate
transition state, designated CuDDC, to be less stable relative
to benzene than chloroform, and the forward rate to be faster in benzene than in chloroform as observed. Such a description relies, of course, on the fact that chloroform is known to hydrogen bond to various ligands, and might be expected to form a stronger inner sphere complex than benzene or toluene. The trends observed in both rates and enthalpies are as the model would predict. Trends in forward $\Delta S_f^*$ values are observed to increase in the same order, perhaps reflecting the situation that chloroform forms a stiffer solvent structure than toluene or benzene through hydrogen bonding.

Although the rate trends are neatly explained at 300°K, a flaw in Rorabacher's argument becomes apparent when the Arrhenius plots for the solvents are examined (fig. 5-12). As the isokinetic relationship would predict (fig. 7-1), above $\sim 340°K$, the observed order of the forward rates reverses itself. In effect, according to Rorabacher's arguments, above this temperature the solvents behave oppositely to that at lower temperatures. Invoking various thermal effects is not a consistent approach, and it would appear that these inner sphere effects discussed by Rorabacher are unable to include isokinetic behaviour.

The consistency of the forward rates for various pyridines in the same solvents is strong evidence that a solvent effect dominates the adduct formation process. In other words, it would appear that the solvents used in this work do not co-ordinate to the metal, but instead form some sort of outer sphere complex.
The replacement of a solvent molecule by the base would then depend only on the solvent structure, and not on the formation of metal-ligand bonds. An inner sphere complex formation cannot be the complete explanation, even using the ideas of Rorabacher just outlined, since negative activation energies are observed for the process. The breaking of a metal-solvent bond would require a positive activation energy. Thus although inner sphere effects may be present, outer sphere effects are more dominant. This point will be elaborated and established shortly.

b) The Bennetto and Caldin Model: It is appropriate at this point to extend the discussion to another dissociative intercharge solvent model, designed to explain certain trends in Ni(II)-bipyridyl reaction with solvent composition. This model, the Bennetto and Caldin model, hereafter referred to as the BC model, has been criticised by Rorabacher as being insufficient in its consideration of inner sphere effects. It is Rorabacher's contention that, although outer sphere effects are present, they are different from those proposed by Bennetto and Caldin in mixed solvents, and inner sphere effects are sufficient to explain the trends in the work of Bennetto and Caldin. It would appear that Rorabacher's inner sphere and outer sphere proposals, as outlined above, do explain previous results in the Ni(II) system reasonably well, but do not include isokinetic behaviour. For the reaction of CuDDC with pyridines in non-coor-
dinating solvents, however, it has already been shown that the isokinetic behaviour should be included. This behaviour is included in the BC model, and a discussion of the model follows.

An ion solvation model first proposed by Frank and Wen was adapted by Bennetto and Caldin to explain certain trends in activation parameters for the Ni(II)-bipyridyl system. The model is illustrated in fig. 7-3.

The central metal ion is surrounded by an inner solvation shell, A, in which it is considered that solvent-solvent forces are defeated by ion-solvent forces. In this respect the "bonding" is considered to be more akin to adsorption of gas molecules than to a crystallisation of solvent about M. The region immediately beyond A, designated B in the figure, is a disordered region of high energy and entropy, relative to the bulk solvent, wherein the solvent molecule may have escaped from the force field of its bulk solvent neighbours, but has not yet penetrated the inner shell, A. The lifetime of a molecule in this disordered region will be short, and the boundaries not well-defined. The outer sphere, C, is composed of bulk solvent when solvent-solvent forces predominate.

A solvent exchange process (ligand exchange or ligand substitution can be considered in an analogous manner) can be readily described in terms of this model. First, a solvent molecule must overcome solvent-solvent forces and escape from C to B (process 1 in the figure). This step can be envisioned as requiring
Fig 7-3: Structural Model for a Solvated Ion
(after Frank and Wen)
Employed by Bennetto and Caldin

A = First Solvated Layer
B = Intermediate Disordered Region
C = Bulk Solvent
an energy comparable to the heat of evaporation, $\Delta H_{\text{vap}}$, for the liquid. A molecule in region B can enter into region A if there is an empty position in A (process 2), which can be created by process 3 in which the inner sphere molecule has overcome the ion-solvent interaction. The "hole" in the bulk solvent is replaced by process 4, which can be regarded as a condensation with energy release $-\Delta H_{\text{vap}}$. The overall free energy of formation, $\Delta G^0$, will have varying contributions from all four processes, and it should be recognized that processes 1 and 4 will be interdependent (process 5) through solvent-solvent interactions and reorganisations. Process 5 can clearly contribute to the energy of the transition state, and it will be shown that this process can, in fact, determine the differences in a common reaction taking place in different solvents.

The energies of the various processes can be identified as follows. If the enthalpy associated with breaking a metal-solvent bond is $\Delta H_{\text{MS}}$, then process 3 refers to $\Delta H_{\text{MS}}$. Processes 1, 4 and 5 can be related to the enthalpy change associated with structural reorganization of the solvent, $\Delta H_{\text{st}}$. It is useful to associate these processes in this manner, but it is difficult to isolate the different contributions to $\Delta H_{\text{st}}$ at present, although qualitative assignments of the overall enthalpy change can be made. The overall relationship for solvent exchange may be expressed as:

$$\Delta H^\neq = \Delta H_{\text{MS}} + \Delta H_{\text{st}}$$
Hence a variation in $\Delta H^*$ can arise through variation of $\Delta H_{st}^{*}$, assuming for the moment that $\Delta H_{MS}^{*}$ remains constant for a series of similar solvents. Variation in $\Delta H_{st}^{*}$ is caused by a balance between processes 1 and 4, whence process 5 is also implicated. If, for example, the structural contributions to $\Delta G^*$ from processes 1 and 4 are approximately equal then no net work is done when molecules enter or leave region C. Under these circumstances $\Delta H_{st}^{*} = 0$. Consequently the reaction is dominated by the dissociative process 3, which can be associated with a metal-ligand bond rupture, as noted earlier. The structure of the bulk solvent remains largely unaffected.

If, now, a solvent is considered whose bulk structure is such that it cannot readily adapt to accommodate the molecule leaving region B (and entering C), then it may be stated that net work must be done on the bulk solvent. This is equivalent to saying that process 1 is contributing to the formation of the transition state. In other terms, the co-operativity (process 5) in the solvent is such that the leaving group cannot enter the bulk solvent (process 4) before an incoming molecule enters B (process 1). Overall, this is tantamount to saying that work has to be done and $\Delta H_{st}^{*}$ will be positive. Alternatively, process 1, being akin to evaporation, is an endothermic one and hence $\Delta H_{st}^{*} > 0$.

In contrast, if the bulk solvent molecules can readily adapt (through, presumably, reorientation and rotation) so that
leaving molecules (process 4) are easily reaccomodated with no work having to be done on the bulk solvent, then $\Delta H_{st}$ will be negative. That is, process 4, the exothermic condensation process, will dominate $\Delta H_{st}$.

The considerations outlined above have been for pure solvents; the effects of mixed solvents or solvent-ligand mixtures may now be mentioned. Obviously the contributions to $\Delta H_{st}$ from processes 1, 4 and 5 will now be modified because of the presence of the ligand (or other solvent molecule). Solvent structures will be modified since a ligand which is not itself the solvent will produce local changes in the liquid structure. These changes will depend on factors like dipole moment and polarisability of the ligand molecule. In other words, factors that may contribute to intermolecular forces. A rough measure of these intermolecular forces is the enthalpy of vaporisation, $\Delta H_{vap}$, and one might expect that the greater the difference between $\Delta H_{vap}$ for the solvent and that for the ligand, the greater the local changes in solvent-ligand mixtures. This fact can be rationalised by noting that a high value of $\Delta H_{vap}$ suggests strong intermolecular forces. Interspersing a solvent or ligand into this structure will change the intermolecular forces considerably. The degree to which the bulk solvent (or solvent mixture) readmits a molecule is its cooperativity.

Thus if processes 1 and 5 remain the same for some solvent, addition of a ligand with a value of $\Delta H_{vap}$ higher than
that of the solvent will lead to a more negative value of $\Delta H_{st}$ since less work is done on the solvent in process 4. This is because the ligand will promote a more ordered and open structure in the solvent. Hence if $\Delta H_{st}$, in this example, is more negative (than in the case of solvent exchange) then $\Delta H^\#$ will be smaller. If $\Delta H_{MS}$ is smaller than $\Delta H_{st}$, then $\Delta H^\#$ will be negative. The more open structure of the solvent will lead to partly compensating effects in $\Delta S_{st}$ and $\Delta S^\#$. It may be considered, then, that the effective $\Delta H_{vap}$ of the solvent-ligand mixture is somewhere between the values for pure solvent and pure ligand.

Now if the addition of the ligand also reduces the ability of the solvent to accommodate a leaving solvent molecule (process 4) then work must be done on the bulk solvent. In other words, process 1 (which is endothermic) and process 5 (which is also endothermic and relates the degree of cooperativity of the solvent to the exchange process) contribute to the formation of the transition state. Hence $\Delta H_{vap}$ effects may be negated by the presence of solvent properties that lead to a low degree of cooperativity. Hydrogen-bonded solvents might be expected to demonstrate these effects.

Discussion of the processes just mentioned in terms of the solvents used in this study requires knowledge of $\Delta H_{vap}$. This is given in Table 7-3.
Before considering the benzene/pyridine system, it should be reemphasised that the solvents used here are essentially non-coordinating. Because of this, it is expected that $\Delta H_{\text{MS}}$ be small, and certainly smaller than $\Delta H_{\text{ML}}$, where $L$ refers to the base in question. Although this latter point is perhaps intuitively obvious, it can also be deduced from the fact that $\Delta H^\dagger_\text{r} > \Delta H^\dagger_\text{f}$. Since $\Delta H_{\text{st}}$ may be assumed the same for both forward and reverse directions, for any given ligand, then from 7-11 $\Delta H_{\text{ML}} > \Delta H_{\text{MS}}$.

Now, for benzene/pyridine mixtures it is known\textsuperscript{132} that $\Delta H_{\text{soln}}$ for pyridine in benzene is $\sim 0$ kcals/mole. It would appear then that very little structure change takes place when pyridine molecules replace benzene molecules. This suggests in turn that for ligand exchange the benzene molecule displaced from the metal ion by the incoming pyridine (processes 3 and 2, respectively) molecule is easily readmitted to the bulk solvent. Process 4, akin to condensation, tends to dominate in this system. Further, $\Delta H_{\text{vap}}$ is greater for pyridine than benzene, and one therefore expects $\Delta H_{\text{st}}$ to be small, or negative. If $\Delta H_{\text{st}}$ is much more negative than $\Delta H_{\text{MS}}$. 

### TABLE 7-3: $\Delta H_{\text{vap}}$ (b.p.) FOR SOLVENTS

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Delta H_{\text{vap}}$ (b.p.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>7.55 kcals/mole</td>
</tr>
<tr>
<td>toluene</td>
<td>8.00 kcals/mole</td>
</tr>
<tr>
<td>chloroform</td>
<td>7.02 kcals/mole</td>
</tr>
<tr>
<td>pyridine</td>
<td>8.37 kcals/mole</td>
</tr>
</tbody>
</table>
is positive, then $\Delta H_f^\#$ will be negative. This is the observed result shown in Table 7-2.

Toluene/pyridine systems are subject to the same criteria, except that now $\Delta H_{\text{vap}}$ for toluene is nearer that of pyridine. In this case, one would expect $\Delta H_f^\#$ for toluene to be larger than that for benzene, assuming similar values of $\Delta H_{\text{MS}}$. This conclusion is further supported by noting that toluene and pyridine are not as similar as benzene and pyridine, hence more work will be required to return toluene to the toluene/pyridine mixture. Thus process 4 will be less exothermic. Overall, Table 7-2 shows $\Delta H_f^\#$ (toluene) > $\Delta H_f^\#$ (benzene), supporting these conclusions.

The pyridine/chloroform case exhibits some interesting applications of the Bennetto/Caldin model. From Table 7-3 it may be noted that the difference in heats of vaporisation for chloroform and pyridine is the largest of the three solvents studied. From the experience gained with toluene and pyridine, then, one expects $\Delta H_{\text{st}}^\#$ to be lowest, or most negative, and hence $\Delta H_f^\#$ to be smallest. However, this conclusion would be wrong, as Table 7-2 indicates. The extra factor to be accounted for here is the strong hydrogen bonding known to exist in chloroform and chloroform/pyridine mixtures. This leads to a large contribution from processes 5 and 1 to the enthalpy of formation of the transition state, since a returning solvent molecule has to do work on the solvent to be reaccommodated. The overall endothermic
contributions from processes 1 and 5 evidently just balance, or slightly outweigh, the contributions from process 4, resulting in chloroform/pyridine mixtures having the largest $\Delta H^\ddagger$, as observed. The fact that the values of $\Delta H^\ddagger$ remain in the same order is further evidence for the concerted processes involved in the mechanistics of ligand exchange or solvent exchange situations, although in this case inner sphere effects are very important. This will be discussed in more detail shortly.

The solvent variation data can be discussed in a slightly different way to that just given, although in terms of the BC model the descriptions are equivalent. For the solvents, the existence of negative activation energies, and the relationship (7-11) allow some qualitative conclusions to be drawn about $\Delta H_{MS}$. Although one might expect some sort of variation of $\Delta H_{MS}$ with solvent, it is not possible at present to evaluate it. As just discussed, this is not really needed since $\Delta H_{vap}$ considerations are more important. Because the solvents studied here are non-coordinating, as opposed to the quite highly coordinating solvents studied by Bennetto and Caldin\textsuperscript{34,160}, and Rorabacher\textsuperscript{35,161}, $\Delta H_{MS}$ is expected to be small. Because of the small variations in coordinating ability for benzene, toluene, and chloroform, one might expect $\Delta H_{MS}$ to show small variations with solvent, but variations negligible compared to $\Delta H_{vap}$, perhaps. The small, almost constant, value of $\Delta H_{MS}$ is therefore a large contributor to the overall negative activation energy for the forward pro-
It can also be mentioned that the evaporation/condensation processes could be likened to an expansion/contraction description of the gas-like region. Such a process would involve entropy differences, and if likened to the gaseous model, a contraction process will be accompanied by a decrease in entropy of the bulk solvent. On an overall basis, passage from processes 1 to 5 in the BC model requires less work to be done against the bulk solvent to reincorporate a solvent molecule than to reincorporate a larger ligand molecule. In the reverse, or dissociation of adduct, direction, the reincorporation of a ligand into the solvent will require more energy than the incorporation of a solvent, leading to an entropy change that should be more positive for reverse reactions than forward ones. This is because the expansion of the outer sphere to reincorporate a ligand molecule is more than that required for a solvent molecule, and a more disordered solvent results. This is the observed trend in these experiments.

For the variation of bases in benzene, examination of base-solvent structure within the BC model would be expected to reveal a trend in $\Delta H_f^\circ$ that reflects the interaction between ligand and solvent. The equality of rates is expected since the same solvent, benzene, is involved and the loss of benzene from the
metal ion is expected to dominate the ligand approach. Trends in $\Delta H_f^\circ$ would be expected, therefore, to reflect steric effects rather than basicity. The most symmetrical base, 4-picoline, will form a better, or tighter, structure with benzene than the other pyridines. A minor contribution from the basicity can be noted in that $\Delta H_f^\circ$ for 4-picoline is greater than that for pyridine. The other picolines show a decreasing $\Delta H_f^\circ$ as the steric effects, represented by the methyl groups, increase. The small variation in rate is also explained (although this variation is not much more than experimental uncertainty) qualitatively in terms of stiffness of solvent structure. Clearly, a fairly bulky 3,4-dimethyl substituent will interfere with the solvent organisation ability, making the benzene/3,4-lutidine more susceptible to the concertion process than the benzene/4-picoline system. The more disordered liquid structure leads to a higher $\Delta S_f^\circ$ for 3,4-lutidine, compared to 4-picoline, also.

These solvent compensation effects, as mentioned earlier, should lead to an isokinetic relationship. The BC model, if correct, should lead to an isokinetic relationship, on the basis of evidence so far. This is hence the evidence for the model for a series of ligand exchange or solvent exchange reactions.

The review by Ritchie and Sager\textsuperscript{165} presents a thorough summary of the factors behind an isokinetic relationship, and will not be repeated here, except to note that processes dominated by solvation effects commonly, if not invariably, show an
isokinetic behaviour. This is because changes in solvent structure demonstrate a balance between entropy and enthalpy such that a change in the structure leads to a compensation in entropy and corresponding compensation in enthalpy. It is not expected, therefore, that $\Delta G$ should reveal very much about solvent, or steric effects, since $\Delta G$ is defined by:

$$\Delta G = \Delta H - T\Delta S$$

A compensation effect, as well-demonstrated by figs. 7-1, 7-2 for the present case, will lead to $\Delta G$ values being almost constant. It then follows that the equilibrium constant, defined as:

$$K = \exp(-\Delta G^*/RT)$$

is a somewhat insensitive, or blunt, tool for studying solvent or ligand effects. Table 7-4 illustrates the values of $\Delta G^*$ obtained.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta G^*$ (kcal/mole)</th>
<th>$\Delta G^f$ (kcal/mole)</th>
<th>$\Delta G^r$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyridine/benzene</td>
<td>0.5</td>
<td>6.1</td>
<td>5.6</td>
</tr>
<tr>
<td>pyridine/toluene</td>
<td>0.6</td>
<td>6.2</td>
<td>5.6</td>
</tr>
<tr>
<td>pyridine/chloroform</td>
<td>0.8</td>
<td>6.3</td>
<td>5.5</td>
</tr>
<tr>
<td>benzene/2-picoline</td>
<td>1.7</td>
<td>7.0</td>
<td>5.3</td>
</tr>
<tr>
<td>benzene/3-picoline</td>
<td>0.4</td>
<td>6.1</td>
<td>5.7</td>
</tr>
<tr>
<td>benzene/4-picoline</td>
<td>0.3</td>
<td>6.2</td>
<td>5.9</td>
</tr>
<tr>
<td>benzene/3,4-lutidine</td>
<td>0.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>
As can be seen, there is remarkably little variation, except for 2-picoline, in the forward direction. There is more variation in the reverse direction, and this point will be reconsidered shortly.

Figure 7-4 shows the correlation between $\Delta H$ and $\Delta S$ for both solvents and bases. The forward correlation is quite significant on several points. First, it establishes that solvent effects do, indeed, dominate the forward formation process, to the extent that even 2-picoline falls on the line. The solvent effects are so well correlated that the BC model is to be considered an excellent description of the mechanistics of ligand and solvent exchange, especially for the forward reaction. Clearly the presence of a common isokinetic temperature means that Rorabacher's inner sphere model must be expanded to include outer sphere effects, otherwise it is incapable of explaining the isokinetic behaviour.

Similar tests of the current theories can be made for the data obtained in the reverse, or dissociative, direction of the reaction between CuDDC and Lewis bases in inert solvents, and conclusions discussed. This will be done now.

C. THE REVERSE, OR DISSOCIATIVE, REACTION:

a) Solvent Effects: The reaction to be considered, common for both solvents and bases, is described by the following:

\[
(7-14) \quad \text{CuDDC} \cdot \text{base} \xrightarrow{k_r} \text{CuDDC} + \text{base}
\]
Fig 7-4: Isokinetic plots for solvents and bases.
• forwards ΔΔ reverse
and clearly involves the breaking of a metal-nitrogen bond, and the dissociation of the adduct, presumably accompanied by resolvation of the CuDDC complex. As Tables 7-1 and 7-2 show, there is not a simple correlation of \( k \) with solvent, but \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) both increase from benzene to toluene.

On the basis of Rorabacher's inner-sphere and outer-sphere mechanisms for a reaction such as (7-14), the solvent molecule must assist in removing the base from the metal. The replacement of the base by a solvent molecule must be determined by the lability of the solvent in the outer sphere. This lability is more enhanced the greater the total solvation energy. Or, the more stable the solvent structure, as for extensive hydrogen bonding solvents, the more likely is a molecule from that solvent to replace the departing ligand\(^{35}\). For CuDDC, inner sphere effects are minimised by the bidentate ligands, leaving one site, most probably, for solvent or ligand co-ordination. Two weak bonds may be formed with solvents, but it seems well established, from the remarks in chapter 5, that only one co-ordinating molecule need be considered. This situation is similar to that wherein Rorabacher used a quinquedentate ligand\(^{35}\) to leave accessible only one co-ordinating site on the Ni(II) ion.

Since chloroform is known to form hydrogen-bonded structures, as does water, it might be expected from Rorabacher's model that the rate of reverse reaction in benzene should be slower than in chloroform. Toluene would be intermediate
because its dipole moment will stiffen the solvent structure somewhat. Table (7-2) indicates that this is the case at 300°K. The presence of an isokinetic plot for the reverse thermodynamic parameters, albeit not as consistent as the forward one, suggests that Rorabacher's prediction will not hold at some other temperature. This is amply illustrated by fig. 5-12.

In the reverse direction, $\Delta H^\text{ML}$, the enthalpy for breaking a metal-ligand bond, is expected to contribute to the overall enthalpy. For pyridine in various solvents, this value should be constant and the trends in $\Delta H^\text{f}$ should reflect $\Delta H^\text{st}$ from (7-11). The trend observed is that $\Delta H^\text{f}$ increases from benzene to chloroform. Hence it would be reasonable to assume that $\Delta H^\text{st}$ increases from benzene to chloroform. This is explained in terms of the BC model by the fact that pyridine does less work in entering the solvent structure of the benzene/pyridine mixture than it does to reenter the chloroform/pyridine structure, but the energy required for a chloroform molecule to leave the strongly interacting pyridine-chloroform solvent structure outweighs the entering process by an amount sufficient to make the process in benzene a lower energy process. The apparent contradiction on the basis of $\Delta H^\text{vap}$ is that the rate is faster in chloroform. This can be rationalised by noting that pyridine dissolves readily in chloroform ($\Delta H^\text{solv} = -1.8 \text{ kcals/mole}$), much more so than benzene. Data is not available for toluene, unfortunately, for, on the basis of this discussion, $\Delta H^\text{solv}$ for pyridine in
toluene should be less favourable than benzene. The easier solvation of pyridine in chloroform would tend to accelerate the leaving of the pyridine molecule more so than for benzene (process 3 in the BC model), on the basis of energetics alone. However, as soon as the pyridine molecule reaches region B a chloroform molecule must replace it (process 1 is still dominant). Similarly for benzene. It is this latter process that is energetically less favourable, leading to the observed trend in enthalpies. The rate in chloroform, however, is still slightly faster than in benzene because for benzene the initial process 3 is the more important in the concerted scheme. One would therefore expect toluene to be resistant, at 300°K, to acceptance of the leaving pyridine molecule, but process 1 in pyridine/toluene to be relatively easy.

It is not easy to see how Rorabacher's outer sphere model might be applied in this case. His associative\(^{35}\) "push" mechanism, whereby the solvent literally "pushes" the ligand from the inner sphere and replaces it with itself is not likely to occur with the bulky solvents and ligands used here. This is, in fact, an objection of his own for methanol\(^{35}\). The dissociative, or "pulling", process mentioned earlier suggests that the more basic solvent will be best at removing the ligand. In this case, the more basic solvent is difficult to ascertain. The criterion that the more labile species in replacing the departed ligand is that with the most solvation energy apparently deter-
mines chloroform as the fastest rate process in the reverse direction, as mentioned before. Rorabacher's work, however, was for co-ordinating solvents, and although his ideas predict the fastest rate, it is difficult to see how non-coordinating solvents, such as those used here, can participate in the enhancement of the leaving rate of a ligand. These bulky solvents could not interact with the nitrogen nucleus, which must be in a sterically crowded environment:

![Diagram](image)

and it is unlikely that chloroform, the most active chemically, could exert a significant "pull" on the ligand. The outer sphere presentation of the BC model seems more likely, based on solvent-ligand and solvent-solvent interactions, as it also explains all the thermodynamic trends, and is apparently more suitable to non-coordinating solvents. The BC model, moreover, allows the equivalence of saying that it is difficult for the ligand to get into the solvent structure, or that the solvent structure is not helpful in removing a ligand.

Disagreements arise, because the BC model predicts that the rate of removal of ammonia from Ni(II) in water should be
faster than in methanol, because of the fact that $\Delta H_{st} > 0$ for methanol and this indicates that methanol will tend to inhibit cooperativity in the transition state. The hydrogen bonding will tend to prevent the ammonia molecule from entering the bulk solvent (processes 4 and 5) before process 1 occurs. Water tends to favour concerted mechanisms, the molecules undergoing highly cooperative molecular motions. Repulsive and attractive intermolecular forces are so strong that as soon as a molecule escapes from the structure, there is a high probability that it will soon return to the structure. Water is unique in that it possesses high stiffness, openness and order, and overall $\Delta H_{st}$ is small. Hence, it would appear that ammonia exchange must be faster in water than in methanol, for instance. Such a prediction is opposite to Rorabacher's findings, and Rorabacher's outer sphere model can explain the results in terms of increased ability for methanol in removing ammonia from Ni(II). That the BC model was postulated on the basis of results for Ni(II)-bipyridyl reactions may have been unfortunate for the application to some other systems.

b) Effects of Varying the Base: With the results of this section, it will be seen that the BC model provides a coherent and consistent interpretation of the results. Referring once again to Table 7-2, the trend of rate constants with base for the reverse direction is seen to follow the order of base
strengths, if it is accepted that 2-picoline is a weaker base than pyridine in benzene for reaction with CuDDC. The trend observed in rates is that expected for the metal-ligand bond breaking order: the stronger the base the harder it is to break the bond, hence the slower the reverse rate. Since the solvent is a common one, $\Delta H_{st}$ is expected to be reasonably constant, except perhaps for small changes caused by interaction of solvent with base. As in the forward direction, process 1 is still a major step in the exchange process, although for solvents entering its contribution is small, energy-wise. For co-ordinating ligands, on the other hand, $\Delta H_{ML}$ will be larger, and positive, and so will contribute to the energetics of the reverse process in a more noticeable fashion.

The trends in $\Delta H_f^\neq$ show a distinct solvent interaction between benzene and the pyridines. In terms of $\Delta H_{MS}$ alone, it would be expected that variation of $\Delta H_f^\neq$ would be with base strength. This is not the case, and the observed trends point out that solvent-ligand structure is important, although $\Delta H_{ML}$ contributions are present. The observed trends indicate that 4-picoline forms a stiffer structure with benzene than do the other pyridines, and hence the work required to remove a solvent from the benzene/4-picoline structure is more than for a more open structure like 3,4-lutidine. The position of pyridine in the trend presumably reflects the fact that pyridine/benzene structures are ordered but not too stiff, thereby per-
mitting easy removal of solvent and easy re-entry of ligand. The base strength, and hence $\Delta H_{ML}$, is lowest, and so pyridine occupies an "anomalous" place in the trend. 2-Picoline, because of steric inhibitions involved with co-ordinating at copper(II) apparently has the highest value of $\Delta H_{ML}$. This seems certainly anomalous, and may reflect an enhanced solvent-ligand interaction, and hence restrictions on the "concerted-ness", or expansion/contraction, of the overall mechanism.

Fig. (7-2) shows the isokinetic plot for bases alone, and fig. (7-4) shows that for all bases and solvents. For the reverse parameters, it is clear that the variation in $\Delta H_{ML}$ must be causing the $\Delta H/\Delta S$ compensation effects to be slightly disturbed. In other words, outer sphere effects alone are not totally sufficient to describe the results, but the lability of the ligand must be included when it is bonded to the metal. It is interesting to note that since 2-picoline behaves approximately like a solvent, an isokinetic line through the points for benzene, toluene, chloroform, and 2-picoline has a better regression coefficient* (0.9996) than the line through the bases alone (0.9979), or the solvents and bases (0.9976). In fact, 2-picoline is on

* the regression, or correlation, coefficient is defined by:

$$R = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}}$$

where $\bar{x}$ indicates the arithmetic mean.
the line through the solvents since the regression coefficient for the three solvents alone (0.9997) is almost unchanged from that including 2-picoline. In contrast, the regression coefficients for the forward plots are much better (see Table 7-5).

TABLE 7-5: REGRESSION COEFFICIENTS FOR ISOKINETIC PLOTS

<table>
<thead>
<tr>
<th>System</th>
<th>R (forward)</th>
<th>R(reverse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>solvents only</td>
<td>0.99999</td>
<td>0.99972</td>
</tr>
<tr>
<td>bases only</td>
<td>0.99995</td>
<td>0.99788</td>
</tr>
<tr>
<td>solvents and bases</td>
<td>0.99988</td>
<td>0.99764</td>
</tr>
<tr>
<td>solvents and 2-picoline</td>
<td>0.99986</td>
<td>0.99957</td>
</tr>
</tbody>
</table>

The solvent-like behaviour of 2-picoline is expected on the basis of the very slow forward rate and small equilibrium constant. It is perhaps the reason for the large positive value for $\Delta H^\circ_T$, which then indicates that large (compared to other pyridines) energies are required to remove solvent from benzene/2-picoline mixtures and to reintroduce a 2-picoline molecule. This pseudo-solvent behaviour should also be reflected by an increase in entropy in the reverse direction, since more disorder is created in both reactants and solvent structure. This is indeed the observation.

With respect to the order of bases on the isokinetic plot,
there is correlation between the dipole moment of the base (Table 7-1) and the order. The isokinetic, hence $\Delta H$, or $\Delta S$, order is:

\[(7-15)\quad 3,4\text{-lutidine} < \text{pyridine} < 3\text{-picoline} < 4\text{-picoline}\]
\[\quad 4\text{-picoline} < (2\text{-picoline}).\]

The dipole moment order is:

\[(7-16)\quad 3,4\text{-lutidine} < (2\text{-picoline}) < \text{pyridine} < 3\text{-picoline}\]
\[\quad 3\text{-picoline} < 4\text{-picoline}\]

Using the BC model, the dipole moment would be expected to reflect solvent structure for a common solvent; the more ordered structure arising from interaction of benzene with the strongest dipole. This correlation is excellent, and is an additional confirmation of the dominance of solvent effects in these reactions.

The emphasis on isokinetic plots here, and by Bennetto and Caldin, deserves some remarks before conclusions are drawn and discussed. It has been pointed out by Ritchie and Sager that simultaneous Hammett (linear free energy relationships, see Appendix 2 for details) and isokinetic behaviour in a series of reactions is rare, and perhaps non-existent. In fact for both relationships to hold there is a quite stringent requirement, that "free energy, entropy and enthalpy must all be separately correlated with the Hammett equation". Laidler's work also suggests that these conditions are difficult to meet. Reaction series giving separate isokinetic or Hammett plots are, of course,
numerous\textsuperscript{127,165}. In this work isokinetic plots have been obtained for the complete system. This infers, then, that no Hammett relationship should be observed. In other words, because $\Delta G^o$ is small, $\Delta G^\neq$ being almost constant, the Hammett equations:

\begin{align}
\text{(7-20)} \quad \log K &= \log K_0 + \sigma \rho \\
\text{(7-21)} \quad \log k &= \log k_0 + \sigma \rho
\end{align}

should not describe any of the results of this work. This is indeed the case, calculations being performed for pyridine as the "parent" compound, using $\sigma$ values\textsuperscript{127} for m- and p-methyl groups on pyridine.
A. GENERAL CONCLUSIONS: In describing fairly detailed studies and results for the overall reaction:

\[(8-1) \quad \text{CuDDC} + B \rightarrow \text{CuDDC}\cdot B\]

in various solvents and with various bases, a number of conclusions have been made. Before detailing these, it might be well to requote Jørgensen's\textsuperscript{183} warning, noted by Langford and Stengle\textsuperscript{181}, that "... kinetics is like medicine or linguistics - it is fascinating, it is useful, but it is too early to hope to understand much of it." Since 1967, however, a great deal of work has been done, and the understanding encompasses a rather larger share now.
Fast exchange processes undoubtedly still pose problems for the kineticist, but it is in the area of neutral molecules and non-coordinating solvents that a great deal of interesting work has yet to be done. As far as is known, this study is the first to be reported in detail for the latter situation. Different theories or interpretations of the results may be applied to future studies. Even with the pronounced agreement between the BC model and this work, questions remain about detailed solvent interactions. For example, in the BC treatment, a "solvent-modified dissociative process"\cite{34}, low values of $\Delta H^\neq$ and $\Delta S^\neq$ can be obtained only if the condensation process dominates. In other words, a negative value of $\Delta H^\text{st}$ is required, as already discussed, to obtain overall negative values of $\Delta H^\neq$, which may be associated with a simultaneous passage of solvent from B to C (in fig. 7-3). Low values of entropy, and corresponding compensating changes in enthalpy, are to be associated with the condensation of a gas.

Why does the condensation process dominate for such reactions? The rationale, assuming this fact, explains the results. Its justification is that process 5 in fig. 7-3 links regions A and C effectively through long range solvent structure, and the vaporisation process is energetically less favourable. Thus one can imagine that process 4 is followed by processes 5 and 1 to complete the solvent, or ligand, exchange. The fact that the forward rate is ligand independent supports the idea that processes 3 and 4 dominate. For very low, for instance negative, $\Delta H^\neq$ values
process 5 obviously does not have much effect and processes 3 and 4 dominate 1 and 2 even more.

This explanation is still a rationale. It remains that the condensation process, assumed equal in magnitude but opposite in sign, to the vaporisation process in setting up the BC model, dominates for these results. The quantitative reason is not really known at present. It can easily be seen that similar considerations might apply to all phases of the solvent contribution to the solvent/ligand exchange situation, depending on the reaction. General conclusions are, however, very useful.

Rorabacher's ideas cannot explain the reversal of rates at the isokinetic temperature. It is evident, also, that CuDDC does not form strong bonds, if any, to the non-coordinating solvents used and therefore whatever inner coordination sphere effects are present are likely to be small. This has been shown to be true for the forward rate, resulting in an excellent isokinetic relationship. For the reverse process small variations in $\Delta H_{\text{ML}}$ are noted when the base is varied and some inner sphere effects contribute. This is reflected in the poorer isokinetic plot for the bases in the reverse direction. Overall, however, the evidence has been shown to overwhelmingly involve outer sphere effects. Thus the Bennetto and Caldin model is most applicable.

The Bennetto/Caldin treatment was derived to account for solvent structure changes, in addition to the breaking of a
metal-solvent, or metal-ligand even, bond, as contributions to the free energy of activation\textsuperscript{34}. Earlier studies have largely managed to avoid this\textsuperscript{34,35}. In applying this model, non-aqueous solvents must be considered in addition to water. The BC model effectively accounts for large variations in enthalpy and entropy. In this work, negative enthalpies of reaction are explained within the framework of the model. Ligand modifications to the solvent can be accounted for and the results obtained here suggest that related series of ligands will stiffen a common solvent proportionately to the dipole moment of the ligand. Steric effects that lead to very low values of $\Delta H_{ML}$ will result in a ligand behaving more as a solvent than a ligand. This is amply illustrated by the behaviour of 2-picoline towards CuDDC in benzene.

The concerted nature of the BC model is a major factor in being able to explain the results of equilibria involving fast processes in non-coordinating solvents. Situations involving charged species in coordinating solvents\textsuperscript{34,35,160-162} are not as sensitive to concerted solvent effects, and it is usually expected in these situations that inner sphere effects are more important\textsuperscript{35}.

In concluding the remarks about the Bennetto and Caldin model, it is sufficient to note that this model completely and consistently explains the results obtained for the process defined by (8-1). Other ideas recently proposed\textsuperscript{35} do not explain
these results sufficiently, and conventional ideas involving solvation pre-equilibria have been shown to be inadequate for this situation. In fact, it has been recently observed that the reaction mechanism:

\[
K_0 \quad (8-2) \quad MS^+_6 + L \overset{\text{fast}}{\rightleftharpoons} MS_6L \quad \overset{\text{slow}}{\rightleftharpoons} MS_5L_x^{(n-m)+} + xS
\]

is of questionable validity in non-aqueous solvents. It should be added that (8-2) may have questionable validity in non-coordinating solvents. The results obtained in this work certainly support this view.

B. **FUTURE WORK:** Application of line broadening effects in epr or nmr spectra to obtain rate constants has been fruitful. Especially so in this work. Further work, however, is limited to relatively few systems if the fast exchange method of analysis is to be employed. Because this method of analysis is convenient, it would seem that future epr work is limited to CuDDC and related dialkylthiocarbamates. If means are available for the analysis of any range of exchange rates, then clearly these studies could be extended to any paramagnetic system with exchange rates between \( \approx 10^5 \) and \( 10^{12} \) sec\(^{-1}\). At the upper limit of exchange rates, consideration of non-secular effects would have to be made, since exchange rates and rotational reorientation times would be similar. Nmr studies might be useful to evaluate some of the unknown solvent effects involved in the
model of Bennetto and Caldin. Nmr studies were attempted on CuDDC in benzene/pyridine and mixed non-coordinating solvents, but chemical shifts observed were very small, and the results inconclusive. This should not deter attempts, using nmr, to study these systems.

In terms of the BC model, it would be instructive to evaluate additional thermodynamic data for several more solvents. Cyclohexane, predicted here earlier to be inert, should yield very low \( \Delta H_f^\# \) values, smaller or more negative than for benzene. The loose solvent structure and the value of \( \Delta H_{vap} \) (7.2 kcals/mole) suggest this. Acetone, on the other hand, should yield larger \( \Delta H_f^\# \) values than chloroform, since it is a coordinating solvent. CuDDC is soluble in both these solvents, but not in methanol or water. Variation of the base to include a few more points would be useful, though not as interesting in terms of the BC model as solvent variations. To test the various solvent-solvent and solvent-ligand interactions best, however, a series of experiments on mixed solvents and mixed ligands should be performed. In this way definite statements about the \( \Delta H_{NS} \) and \( \Delta H_{st} \) terms may be forthcoming, which would shed considerable light on the significance of liquid structure in fast reactions in non-coordinating solvents.
A. **Sample Preparation:** The analysis of epr line positions and linewidths for copper in solution is often severely complicated by the presence of two isotopes in naturally-abundant copper. Copper-63 and copper-65 isotopes are present in a 70%:30% ratio, respectively. For samples showing narrow linewidths, resolution of the two isotopes is readily achieved in many solutions. CuDDC epr spectra show these effects, and hence it was decided to perform the experiments with 99%+ copper-63. The isotopically pure metal was obtained from A.E.R.E., Harwell, England.

Pure copper metal was converted to copper(II) nitrate in reagent-grade nitric acid. The nitrate anions were replaced with chloride anions by repeated reaction with hydrochloric acid.
The cupric chloride so obtained was washed repeatedly with de-ionized water, and green-blue crystals of Cu\(^{63}\)Cl\(_2\).2H\(_2\)O obtained. This product was reacted with a slight excess of sodium diethyl-dithiocarbamate (Eastman) in absolute ethanol. The resultant dark green, almost black, precipitate was filtered, washed with ethanol and ether, dried, and recrystallised several times from benzene. This procedure yields shiny dark green needles of copper(II) bis(diethyldithiocarbamate) in high yield (\(\sim 92\%\)). Analysis showed (theoretical percentages in parentheses) the following percentage composition: C - 33.26 (33.43), H - 5.87 (5.57), and N - 7.78 (7.80).

\(^{63}\)CuDDC was kept dry in a dessiccator during the investigation, although it has been noted\(^{114}\) that copper(II) \(\beta\)-diketonates and related compounds are normally obtained anhydrous and show no tendency to coordinate atmospheric moisture. No difference in the epr signal was noted in this work between the dry CuDDC and that which was left exposed to air for several weeks.

CuDDC prepared from naturally-occurring CuCl\(_2\).2H\(_2\)O was prepared in the same manner as \(^{63}\)CuDDC, and used for situations where the presence of the two isotopes was unimportant. Resolution of the high-field epr line into two peaks confirmed the presence of the two isotopes in a 2.3:1 ratio.

All solvents used in this work: benzene, toluene, chloroform, carbon tetrachloride, cyclohexane and acetone were of spectroscopic grade quality (Fisher), which were kept sealed
before use. After opening, the solvents were stored under dry nitrogen and over Linde 4A molecular sieves, if they were to be reused. Attempts were made, in all cases, to use opened bottles only for a day or less, so as to minimise any absorption of atmospheric impurities. Nmr spectra of benzene, toluene, and chloroform indicated no appreciable impurity content.

All organic bases used; piperidine, pyridine, 2,6-lutidine, 2,4-lutidine, 2-, 3-, and 4-picoline were of highest available purity. Gas chromatographic analysis failed to show any impurities in the lutidines and picolines, although it must be noted that these isomers are difficult to resolve amongst themselves, and the gas chromatographic separation might not reveal isomeric impurities. The presence of an appreciable amount of impurity that might interfere in the exchange process should be resolvable by epr spectra taken of CuDDC in the neat solvents. In all cases, high gain epr spectra failed to show any sign of impurity, although they did partially show hyperfine splittings from sulfur-33 (0.7% natural abundance). As with the solvents, the bases were kept cool and dry before use, at which time they were resealed under nitrogen with an appropriate drying agent (see, for example, L.E. Tenenbaum, in "The Chemistry of Heterocyclic Compounds", Interscience, New York (1961), volume 14, section 2).

All solutions prepared from CuDDC in the various solvent/base mixtures were stable once prepared and degassed, and showed
no tendency to precipitate. The least squares analysis used in this work required a range of concentrations of base in any particular solvent usually calculated as a minimum of three times the number of variables used in the least squares fit. Since three parameters were varied, on average, at least nine concentrations were prepared for each system. Once the range of concentrations to be covered was determined, solutions were made up individually, CuDDC dissolved in them, and a sample transferred to a silica epr tube. This solution was freeze-thaw degassed a number of times on a vacuum system, and then dry nitrogen introduced to approximately atmospheric pressure to maintain normal boiling and freezing points of the solvent mixtures. Epr spectra were then recorded over a range of temperatures. All spectra were recorded within a similar period of time to ensure consistency. No decomposition over a period of several days was noted in any of the samples mentioned so far.

Decomposition, or reaction, did occur in piperidine and piperidine/solvent systems, and in the carbon tetrachloride/pyridine system. The result was a diamagnetic pale green solution in all cases (CuDDC in solution is normally yellow-brown in colour). In a piperidine/benzene system that was being recorded by epr it was noted that during the decomposition, whilst no solution colour change was yet discernible, a free radical spectrum of several lines was observed, coincident with the much broader and larger high field line of the CuDDC spectrum. As
the solution decomposed further and changed colour, all epr signals decayed. This free radical spectrum was then obtained independently by reacting piperidine with AlCl₃ in an appropriate solvent, and it could be observed to consist of eleven lines. The interpretation is not entirely clear, but the spectrum appears to be due to hyperfine splittings from a nitrogen nucleus and four equivalent protons.

All epr solutions were prepared to be between $10^{-4}$ and $5 \times 10^{-4}$ M in CuDDC. No broadening due to dipolar effects is discernible in this region, and strong epr signals are readily attained.

Solutions for UV spectroscopy were prepared using naturally-occurring copper(II), and oxygen removed by bubbling nitrogen through for a reasonable period. Matched quartz cells of 1 cm pathlength were used throughout.

B. INSTRUMENTAL METHODS: Epr spectra were recorded on a Varian E-3 spectrometer equipped with a four inch magnet and using 100 KHz field modulation. For all spectra recorded the same X-band cavity was used, and all Fieldial, modulation amplitude and scan time settings were the same. Field calibration was by means of a proton magnetometer manufactured in this department. The probe for the magnetometer was connected to an oscillator which supplied a variable frequency of $\sim 14$ MHz (X-band fields), modulated at 20 Hz. After beating with a signal generator the proton re-
sonance frequency was monitored on a Hewlett Packard 5425L frequency counter equipped with a 3-12 GHz plug-in unit to measure microwave frequency. Microwave frequency was monitored several times during each scan, so as to be able to reject any spectra recorded during unstable conditions. Absolute field measurements to ± 0.2 gauss and frequency measurements to ± 20 KHz were made.

Temperature control was effected using a Varian V6040 control unit, with a special dewar containing the sensor and heater. This device was calibrated with a copper-constantan thermocouple. All samples were continuously monitored for temperature fluctuations, the thermocouple junction being placed beside the sample tube and as far into the cavity as was possible without interfering with the cavity tuning. It was found impossible to place the thermocouple junction at the center of the cavity with the sample, so the temperature difference between the center and the junction was measured before and after a scan to correct the actual sample temperature. This temperature difference was a nearly constant 0.5°C. Checks were made on the difference between the sample temperature measured in the liquid itself, and outside at the wall of the silica tube. No appreciable difference was found. During an actual scan temperature fluctuation was never more than ± 0.2°C, and absolute thermocouple measurements were determined, by comparison with boiling and slush points of water,
to be accurate to at least ± 0.05°C.

UV spectra were recorded on a Cary 14 instrument equipped with an R-213 phototube.

Concentrations are subject to weighing and volumetric errors. Weighing errors are ± 0.01 mg, causing essentially negligible error in weighings of ~ 3 - 5 mg. Volumetric measurements were made wholly with graduated pipettes which can be considered accurate to ~ 0.4% or better\textsuperscript{119}. Concentrations of various samples should therefore be subject to an uncertainty ~ 1% or less. Since all concentrations were calculated for room temperature densities and volumes, corrections for temperature, on the basis of density changes alone, were calculated. Over the range 0 - 60°C, used here, the temperature corrections are negligible for very low concentrations, but become significant for higher concentrations. An 8M solution of pyridine, in benzene, for example, is in reality 7.7M at 60°C. When significant corrections were made to the concentrations, although it was found that the least squares results were not overly sensitive to such changes, since the analysis is, in effect, similar to an averaging over a series of concentrations.

C. DATA ANALYSIS: Various steps in the analysis procedure were all carried out using a series of least squares fitting routines and the U.B.C. IBM 360/67 computer. The least squares fitting program involves an appropriate routine containing the differen-
tials of the function to be analysed, and the least-squares variation is carried out using a fast iterative matrix inversion and diagonalisation procedure to obtain the variables and standard deviations. Iteration continues until the standard deviations are reduced to an appropriate tolerance.

The four epr line positions for each spectrum were fitted to Bleaney's equation\textsuperscript{120}, to second order in \(a_0\) and \(g_0\):

\[
H(m_I) = \frac{g_e}{g_0} H_0 - a_0 M_I - \frac{a_0}{2H(m_I)} \left\{ I(I + 1) - m_I^2 \right\}
\]

where the various terms have their usual meaning\textsuperscript{120}.

Because there are four lines and only two variables a consistent fit was obtained very rapidly, with deviations in \(g_0\) and \(a_0\) being \(\pm 0.0001\) and \(\pm 0.05\), respectively.

Since the whole spectrum shows the effects of chemical exchange, any one of the four lines could be analysed for the exchange parameters. In practice, however, only the +1/2 and +3/2 lines are narrow enough to satisfy the linewidth criteria of (2-28). Both lines were analysed for the benzene/pyridine system, to establish the procedure, and also for the other two solvents with pyridine, although in these latter examples only the results for the +3/2 line are quoted. The results are essentially equivalent for both lines, the equilibrium constants being identical, for instance. Because the non-exchange widths for the +1/2 line are broader than for the +3/2 line, however, it was
noted that the least squares fitting procedure was not as consistent in the +1/2 case as the +3/2 case. This was especially true at low temperatures. Thus it was decided to carry out the analysis for the +3/2 line in all cases. This means that the larger $\omega_A - \omega_B$ for this line might cause additional problems, leading to a larger exchange effect on the +3/2 line compared to all others, however. Careful application of the fitting procedure, however, revealed that overall the +3/2 line data gives most consistent results and is most consistently within the fast exchange limitations outlined in (2-28).

Measured peak-to-peak linewidths, $\Delta H$, were corrected for possible modulation broadening using an iterative procedure based on an equation developed by Wahlquist\textsuperscript{121}. The modulation-broadened linewidth, $\Delta H$, is related to the true linewidth, $\Delta H_t$, by:

$$
(9-2) \quad \Delta H = \Delta H_t \left\{ R^2 + 5 - 2(4 + R^2)^{1/2} \right\}^{1/2}
$$

where $R = H_m/\Delta H_t$ and $H_m$ is the amplitude of the modulation field.

A useful rule of thumb\textsuperscript{95} is that to avoid broadening, $H_m$ should be less than one tenth $\Delta H$, although for this work $H_m \leq \Delta H/3$ appears to be sufficient for most cases. A modulation amplitude of 1 G was used throughout this work and no significant corrections using (9-2) were found for widths above 5 G. Tables 9-1 and 9-2 illustrate the corrections calculated. The 100 KHz modulation frequency associated with $H_m$ contributes a constant broadening of $\pm 35$ mG, or 70 mG overall, to the epr spectra.
TABLE 9-1: EFFECTS OF MODULATION ON OBSERVED LINewidth, FROM WAHLQUIST\textsuperscript{73}

<table>
<thead>
<tr>
<th>$\Delta H_{pp}^{obs}$ (G)</th>
<th>$\Delta H_{pp}$ (G)</th>
<th>$\Delta H_{pp}^{obs}$ (G)</th>
<th>$\Delta H_{pp}$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.67</td>
<td>6.0</td>
<td>5.96</td>
</tr>
<tr>
<td>2.0</td>
<td>1.87</td>
<td>7.0</td>
<td>6.96</td>
</tr>
<tr>
<td>2.5</td>
<td>2.40</td>
<td>8.0</td>
<td>7.97</td>
</tr>
<tr>
<td>3.0</td>
<td>2.91</td>
<td>9.0</td>
<td>8.97</td>
</tr>
<tr>
<td>3.5</td>
<td>3.43</td>
<td>10.0</td>
<td>9.97</td>
</tr>
<tr>
<td>4.0</td>
<td>3.94</td>
<td>15.0</td>
<td>14.98</td>
</tr>
<tr>
<td>5.0</td>
<td>4.95</td>
<td>20.0</td>
<td>19.99</td>
</tr>
</tbody>
</table>

TABLE 9-2: EFFECTS OF DIFFERENT MODULATION AMPLITUDES ON AN OBSERVED LINewidth OF:

(i) 3.0 G

<table>
<thead>
<tr>
<th>$H_m$ (G)</th>
<th>$\Delta H_{pp}$ (G)</th>
<th>(ii) $H_m$ (G)</th>
<th>$\Delta H_{pp}$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>3.00</td>
<td>0.2</td>
<td>5.50</td>
</tr>
<tr>
<td>0.4</td>
<td>2.99</td>
<td>0.4</td>
<td>5.49</td>
</tr>
<tr>
<td>0.6</td>
<td>2.97</td>
<td>0.6</td>
<td>5.48</td>
</tr>
<tr>
<td>0.8</td>
<td>2.95</td>
<td>0.8</td>
<td>5.47</td>
</tr>
<tr>
<td>1.0</td>
<td>2.91</td>
<td>1.0</td>
<td>5.45</td>
</tr>
<tr>
<td>2.0</td>
<td>2.63</td>
<td>2.0</td>
<td>5.31</td>
</tr>
<tr>
<td>3.0</td>
<td>2.00</td>
<td>3.0</td>
<td>5.07</td>
</tr>
</tbody>
</table>

|           |                  | 4.0            | 4.68             |
|           |                  | 5.0            | 4.09             |
The line positions obtained from (9-1) were analysed using:

\[
\langle \omega \rangle = \frac{\omega_A}{1 + K[L_o]} + \frac{K[L_o] \omega_B}{1 + K[L_o]}
\]

by least squares fitting the observed line positions, \( \langle \omega \rangle \), to those calculated from (9-3). \( K, \omega_A \) and \( \omega_B \) were allowed to vary, with \([L_o]\) the independent variable, until a consistent fit was obtained. Initial estimates of \( \omega_A \) and \( \omega_B \) were those values measured in neat solvents. Since both \( g_o \) and \( a_o \) are temperature dependent, values of \( \omega_A \) and \( \omega_B \) were, as measured in neat solvents. The difference is also temperature dependent. This dependence was included in the least squares procedure in the initial estimates of \( \omega_A \) and \( \omega_B \), and fitted values of these parameters reflected these findings, although it was noted that fitted values of \( \omega_B \) were almost temperature-independent in some cases. This is undoubtedly because these fitted \( \omega_B \) values represent an extrapolation of \( \langle \omega \rangle \) to infinite base concentration, whereas the neat solvent values are obtained in concentrations of base \( \sim 12 \text{ M} \), where 100% adduct formation is never attained. This large extrapolation would be expected to render the \( \omega_B \)'s relatively insensitive to temperature. This is not the case with \( \omega_A \) values.

From the standard deviations in the fitted results, uncertainties in \( K \) can be estimated to be \( \pm 0.02 \text{ l/mole} \) and in \( \omega_1 \) as \( \pm 0.0005 \text{ sec}^{-1} \). Standard deviations are calculated according to usual methods \( ^{122,123} \).
The temperature dependence of $K$, as discussed earlier and in Appendix 1, is described by the Arrhenius relationship:

$$K = \exp(-E_a/RT)$$

A straight line obtained from a plot of $\ln K$ vs. $1/T$ will have slope $-E_a/R$, and errors associated with the slope, intercept, and any point on the line can be evaluated by standard procedures. In this work it was assumed that the temperature was subject to much smaller error than $K$, or $k$, and hence was regarded as measurable without error. This results in a simplification of the error analysis, and standard deviations of any point $Y_0$ on the straight line at $x = x_0$ can be calculated from:

$$s_{Y_0} = s \left( \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum (x_i - \bar{x})^2} \right)^{1/2}$$

where $s$ is the standard deviation of the parameters subject to error, $y_i$, $\bar{x}$ is the mean of the $x$ values, $n$ the number of points on the line. By using (9-5) errors in $\ln k$, for instance, can be estimated, and typical standard deviations are $\sim 0.1 - 0.14$, which, at $300^\circ K$, lead to uncertainties in $k \sim 0.2 \times 10^8$ sec$^{-1}$. This is of the order of the experimental error in $k$, resulting from uncertainties involved in measuring $\gamma$. Experimentally-obtained linewidths were least squares fitted to the expression:
\[(9-6)\] 
\[T_{2A}^{-1} = p_A T_{2A}^{-1} + p_B T_{2B}^{-1} + p_B^2 T_{2B} \left[ \omega_A \omega_B \right]^2 \]
\[+ \frac{p_B}{\tau_B} \left\{ (p_A - p_B) \delta (3 \Delta^2 - \delta^2) + (5p_A p_B - 1) (\Delta^4 - 6 \delta^2 \Delta^2 + \delta^4) \right\} \]
\[+ \frac{p_B^2}{\tau_B} \left\{ \frac{1}{2} \frac{1}{I(1+I) - \omega^2} \left[ \frac{1}{\omega} \frac{2}{2} \frac{2}{2} I \right] \left( a_A - a_B \right)^2 \right\} \]

where the first line is the usual modified Bloch result for fast exchange, (4-4), the second line the slow exchange corrections of Corden and Rieger, (4-5), and the third line the non-secular contributions calculated from relaxation-matrix theory, (4-11).

The last two terms in (9-6) are usually very much smaller than the first, in the experiments performed here. Exceptions could occur at low temperature and/or high base strength or formation constant \((K \geq \gamma)\). Table 9-3 illustrates the comparison.

Using values of \(K\) and \(\omega_A - \omega_B\) obtained from the line position fitting procedure, a least squares fit of observed to calculated linewidths using (9-6) was made using linewidths measured in neat solvents, at each temperature, as initial estimates of \(T_{2A}^{-1}\) and \(T_{2B}^{-1}\). Free variation of \(T_{2A}^{-1}\), \(T_{2B}^{-1}\) and \(\tau_B\) allowed \(k_r = \frac{\gamma}{\tau_B}\) and \(k_f = K k_r\) to be calculated. Trends in the fitted linewidths, \(T_{2A}^{-1}\) and \(T_{2B}^{-1}\), reflected those of the observed values, but these parameters were not used for any other specific calculations, and hence are not considered in any detail. Maximum uncertainties in \(\tau_B\) were found to \(\pm 0.15 \times 10^{-9}\) sec, leading to experimental uncertainty in \(k_r \approx \pm 0.2 \times 10^8\) sec\(^{-1}\). Uncertainties in various derived
<table>
<thead>
<tr>
<th>Base Concentration (M)</th>
<th>Ordinary Bloch Term</th>
<th>Extended Bloch Term</th>
<th>Non-Secular Term</th>
<th>$T_2^{-1}$ (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.03</td>
<td>$1.198 \times 10^8$ sec$^{-1}$</td>
<td>$0.418 \times 10^6$ sec$^{-1}$</td>
<td>$0.171 \times 10^4$ sec$^{-1}$</td>
<td>$1.202 \times 10^8$ sec$^{-1}$</td>
</tr>
<tr>
<td>1.38</td>
<td>$1.156 \times 10^8$ sec$^{-1}$</td>
<td>$3.046 \times 10^6$ sec$^{-1}$</td>
<td>$0.233 \times 10^4$ sec$^{-1}$</td>
<td>$1.187 \times 10^8$ sec$^{-1}$</td>
</tr>
<tr>
<td>2.77</td>
<td>$1.036 \times 10^8$ sec$^{-1}$</td>
<td>$2.060 \times 10^6$ sec$^{-1}$</td>
<td>$0.364 \times 10^4$ sec$^{-1}$</td>
<td>$1.056 \times 10^8$ sec$^{-1}$</td>
</tr>
<tr>
<td>3.55</td>
<td>$0.887 \times 10^8$ sec$^{-1}$</td>
<td>$0.457 \times 10^6$ sec$^{-1}$</td>
<td>$0.588 \times 10^4$ sec$^{-1}$</td>
<td>$0.891 \times 10^8$ sec$^{-1}$</td>
</tr>
<tr>
<td>6.20</td>
<td>$0.762 \times 10^8$ sec$^{-1}$</td>
<td>$0.012 \times 10^6$ sec$^{-1}$</td>
<td>$0.950 \times 10^4$ sec$^{-1}$</td>
<td>$0.762 \times 10^8$ sec$^{-1}$</td>
</tr>
<tr>
<td>7.79</td>
<td>$0.736 \times 10^8$ sec$^{-1}$</td>
<td>$-0.006 \times 10^6$ sec$^{-1}$</td>
<td>$1.086 \times 10^4$ sec$^{-1}$</td>
<td>$0.736 \times 10^8$ sec$^{-1}$</td>
</tr>
<tr>
<td>12.41</td>
<td>$0.717 \times 10^8$ sec$^{-1}$</td>
<td>$-0.011 \times 10^6$ sec$^{-1}$</td>
<td>$1.067 \times 10^4$ sec$^{-1}$</td>
<td>$0.717 \times 10^8$ sec$^{-1}$</td>
</tr>
</tbody>
</table>
parameters are as shown in tables of results, unless otherwise stated.
REFERENCES


120. B. Bleaney, Phil, Mag. 42 441 (1951).


166. K.J. Laidler, Trans. Faraday Soc. 55 1725 (1959) and following papers.


APPENDIX 1: The Arrhenius Law:

Basically, Arrhenius' Law states\(^1,2\) that only activated (or energised) molecules undergo chemical change. Formulation of this principle requires two experimental relationships, defined at equilibrium: one,

\[(\text{A1-1}) \quad K = \frac{k_1}{k_2}\]

where \(K\) is the equilibrium constant, \(k_1\) and \(k_2\) the forward and reverse rate constants, for a simple process, and,

\[(\text{A1-2}) \quad \Delta H^o = RT \frac{d \ln K}{dT}_p\]

where \(\Delta H^o\) is the overall heat of reaction, \(R\) the gas constant, and the subscript \(p\) denotes constant pressure.

Combining A1-1 and A1-2 yields:

\[(\text{A1-3}) \quad \begin{cases} \frac{RT^2(d \ln K)}{dT}_p = \frac{RT^2(d \ln k_1)}{dT}_p - \frac{RT^2(d \ln k_2)}{dT}_p \\ \text{or, more simply, } \Delta H^o = E_{A,1} - E_{A,2} \end{cases}\]

where the \(E_{A,1}\) are the apparent activation energies for the process. Combining A1-3 and A1-2 gives further:

\[(\text{A1-4}) \quad \left(\frac{RT^2(d \ln K)}{dT}_p - \Delta H^o\right) = \left[\frac{RT^2(d \ln k_1)}{dT}_p - E_{A,1}\right] - \left[\frac{RT^2(d \ln k_2)}{dT}_p - E_{A,2}\right].\]

Now the LHS is zero, by definition. Arrhenius' contribu-
tion was that each of the bracketed terms on the RHS is also zero, and so the forward and reverse reactions can be considered separately. One thus obtains:

\[ (A1-5) \quad E_A = RT^2 \left( \frac{d \ln k}{dT} \right)_p \]

or,

\[ (A1-6) \quad E_A = -R \left( \frac{d \ln k}{d(1/T)} \right)_p \]

which is the form most often seen. If, in fact, the activation energy \( E_A \) is considered constant over the temperature range being studied, \( A1-6 \) may be integrated to give:

\[ (A1-7) \quad k = A \exp(-E_A/RT) \]

This form is thus more restricted than that of \( A1-6 \), and is the form originally proposed by van't Hoff\(^3\), based on experimental results of Hood\(^4\), who proposed the empirical law:

\[ (A1-8) \quad \log k = B - A'/T, \quad A' \text{ and } B \text{ being constants.} \]

The integrated form of \( A1-7 \) is, in fact:

\[ (A1-9) \quad \ln k = A - \frac{E_A}{RT} \]

where \( A \) is a constant often called a frequency factor (although it has units of frequency only for a first-order reaction). Hence a plot of \( \ln k \) vs. \( 1/T \) will be linear with slope \(-E_A/R\) and
intercept $A$ (at $T = 0$) if the reaction being considered has Arrhenius' temperature-dependence. The law is obeyed for many chemical reactions. Sometimes the more general law:

$$k = AT^n e^{-E_a/RT}$$

is invoked, where $n$ has any value dictated by experiment. The Arrhenius law finds wide application in chemistry and is quite successful. Several unusual applications of the law have been given by Laidler$^7$.

Frequently it is convenient, in solution especially, to express the experimental, or Arrhenius, energy of activation in terms of thermodynamical functions. This is accomplished by first noting that the activated complex (the energy of activation is that required to go from the initial state to the activated state) is in equilibrium with the reactants. In other words:

$$A + B \rightleftharpoons X^\#$$

where $X^\#$ represents the activated complex. Thus an equilibrium constant $K^\#$ can be defined for Al-11, and the overall forward rate of the reaction:

$$A + B \rightleftharpoons X^\# \rightarrow C$$

can be shown$^1$ to be related to $K^\#$ by:

$$k = \frac{k^\#T}{h} K^\#$$
where \( k'T/h \) represents a Boltzmann population constant.

Now, from thermodynamics, the equilibrium constant \( K^\# \) can be related to the Gibbs free energy increase in going from the initial state to the activated state \(^6\):

\[
K^\# = e^{-\Delta G^\#/RT}
\]

so one may write:

\[
k = \frac{k'T}{h} \ e^{-\Delta G^\#/RT}
\]

Since it is now possible to write:

\[
\Delta G^\# = \Delta H^\# - TS^\#
\]

then

\[
k = \frac{k'T}{h} \ e^{-\Delta H^\#/RT} e^{\Delta S^\#/R}.
\]

which is that of Wynne-Jones and Eyring \(^5\).

For unimolecular reactions, or reactions in solution, it can be assumed that there is no change in the number of molecules as the activated complex is formed, and the experimental energy of activation may be written:

\[
E_{exp} = \Delta H^\# + RT
\]

Hence knowing the value of \( E_{exp} \) from a simple Arrhenius plot (eq. A1-9), \( \Delta H^\# \) is available. The Boltzmann constant term in eq. A1-17 can be evaluated next at some desired temperature, and hence \( \Delta S^\# \) derived at that temperature. \( \Delta G^\# \) is then avail-
able from Al-16.

Although the Arrhenius equation is largely successful in explaining the temperature dependence of equilibrium and rate constants, there are many potential exceptions, one of which is fast reactions. The temperature independence of the activation energy is clearly useful only when $E_{\text{exp}} \gg RT$ in eq. Al-18. Many of these objections are thoroughly discussed by Caldin.\textsuperscript{8} Also, Labhart points out that for $E_{\text{exp}} \sim RT$, conclusions as to what $E_{\text{exp}}$ defines cannot be made, although if a linear Arrhenius plot is obtained, and if $E_{\text{exp}}$ is not close to RT, then careful interpretation of $E_{\text{exp}}$ does yield useful results. To consider a "break" in the Arrhenius plot as evidence for the superposition of two mechanisms with different activation energies is an interpretation that may be wrong in these low energy regions.

References:

3. J.H. van't Hoff, "Etudes de Dynamique Chimique", Muller, Amsterdam (1884).
4. J.J. Hood, Phil. Mag. 20 323 (1885).


APPENDIX 2: Linear Free Energy Relations and Isokinetic Plots.

A number of quantitative relationships have been suggested in connection with the effects of substituents on the rates of reactions. These are well documented by Ritchie and Sager. For the present very brief discussion, the derivation of Hammett will be outlined.

The relationship applies to a series of aromatic compounds with a reactive side chain and a substituent m- or p- to it. Ortho substituents are not considered because of steric interactions. For example, a group of substituted benzoic esters is often used. Accordingly, a rate or equilibrium constant for reaction of any of these compounds is related to the value for an unsubstituted (parent) member of the series in terms of two parameters: the substituent parameter \( \sigma \) and the reaction constant \( \rho \), which depends on external conditions, such as the solvent. Thus one usually writes:

\[
\text{(A2-1)} \quad \log k = \log k_0 + \sigma \rho
\]

or

\[
\text{(A2-2)} \quad \log K = \log K_0 + \sigma \rho
\]

By arbitrarily assigning \( \rho \) for benzoic acid to be unity, for the ionization equilibrium constant in aqueous solution, and for the substituted benzoic acids, \( \sigma \) is the logarithm of the
ratio of the ionization constant of a substituted benzoic acid to that of benzoic acid itself. Thus a series of \( \sigma \) values can be determined from this control series, and they have been largely successful when applied correctly\(^1,3\).

Now the Hammett relationships can be shown to be equivalent to linear relationships between the free energies of reaction or activation for different series of reactions.

As noted in Appendix 1, one may write:

\[
(A2-3) \quad k = \frac{k'T}{h} e^{-\frac{\Delta G^f}{RT}}
\]

so that taking natural logarithms yields:

\[
(A2-4) \quad \ln k = \ln \frac{k'T}{h} - \frac{\Delta G^f}{RT}
\]

Substituting into A2-1 gives:

\[
(A2-5) \quad \Delta G^f = \Delta G^f_0 - RT\rho \sigma
\]

Eq. A2-5 applies to any reaction involving a reactant having a series of substituents, and a particular value of \( \rho \) can be assigned. Now for a second series of homologous reactions, having a different reaction constant \( \rho' \),

\[
9A2-6) \quad \Delta G'^f = \Delta G'^f_0 - RT\rho' \sigma
\]

Dividing eqs. A2-5 and A2-6 by \( \rho \) and \( \rho' \), respectively, then subtracting, yields:

\[
(A2-7) \quad \frac{\Delta G^f}{\rho} - \frac{\Delta G'^f}{\rho'} = \frac{\Delta G^f_0}{\rho} - \frac{\Delta G'^f_0}{\rho'}
\]
or

\[ \Delta G^\# = \frac{\rho}{\rho}, \Delta G^{\#} = \text{constant} \]

Equation A2-8 is a linear relationship between the free energies of activation for two homologous series of reactions. These linear relationships have been observed for a large number of examples\(^1,3\).

Now, it has often been argued that the presence of a linear free energy relationship was associated with a linear relationship between the enthalpies of activation and energies of reaction, the entropies remaining constant. It is now established\(^1,3,4\) that, on the contrary, the free energies are much simpler functions than the enthalpies and entropies, which are more sensitive to external factors (i.e. solvent). Many examples are known that exhibit linear free energy relationships, but no clear enthalpy and entropy relationships. This is possible because of a "compensating effect", or isokinetic relationship, wherein the entropy and enthalpy change so as to compensate each other. Plots of \( T\Delta S^\# \) against \( \Delta H^\# \), where such an effect holds, yield straight lines of slope approximately unity. Or, as is often done, plots of \( \Delta S^\# \) against \( \Delta H^\# \) yield a slope known as the isokinetic temperature, \( T \).

These isokinetic relationships are only very rarely, if at all, observed when there is a linear free energy relationship, and are most often noted for a given reaction in a series
of solvents, or for homologous reactions in which substituents are introduced into a reactant. It actually follows that if there is a linear relationship between $\Delta H^\neq$ and $\Delta S^\neq$, then, since $\Delta G^\neq = -T\Delta S^\neq + \Delta H^\neq$ there can be no linear free energy relationship. Those reactions that have been claimed to exhibit both relationships are most likely the result of experimental error.

When isokinetic relationships are found for overall processes in solution, the explanation cannot be explained in terms of purely kinetic effects, but solute-solvent interactions must play a large part. For example, Laidler states that any effect leading to stronger solvent-solute interaction will lower the enthalpy, and also, by restricting solvent vibrational and rotational freedom, lower the entropy. A very small effect on $\Delta G$ usually results.

References