ELECTRON SPIN RESONANCE STUDIES OF THE LIGAND EXCHANGE IN CUPRIC COMPLEXES WITH DIETHYLDITHIOCARBAMATE AND DIETHYLDITHIO-PHOSPHATE AS LIGANDS*

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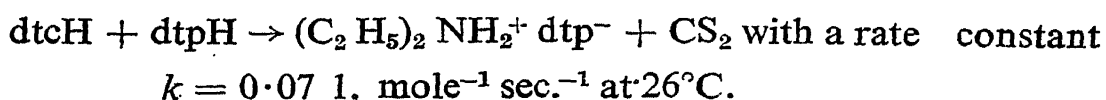(*Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay-5*)

ABSTRACT

The kinetics of ligand substitutions in the cupric complexes where a diethyldithiocarbamate (dtc^-) is replaced by a diethyldithiophosphate (dtp^-) has been studied with chloroform as solvent. The relative concentrations of the paramagnetic species produced in the reactions have been determined using electron spin resonance. The reaction studies suggest the presence of the short time equilibria:

$$Cu\,(dtc)_2 + dtpH \rightleftharpoons Cu\,(dtc)\,(dtp) + dtcH$$

$$Cu\,(dtc)\,(dtp) + dtpH \rightleftharpoons Cu\,(dtp)_2 + dtcH$$
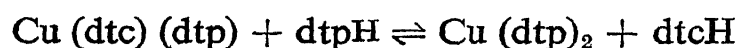
where the equilibrium constants have the value, $0 \cdot 0625$ and $0 \cdot 00143$ respectively. The equilibria are disturbed by the reaction:

$$dtcH + dtpH \rightarrow (C_2H_5)_2\,NH_2^+\,dtp^- + CS_2 \text{ with a rate} \quad \text{constant}$$

$$k = 0 \cdot 07 \text{ 1. mole}^{-1}\text{ sec.}^{-1} \text{ at } 26°C.$$

Analysis of the thermodynamic parameters determined from the study of the kinetics of the reactions at various temperatures shows that dtp^- group favours more solvent and excess ligand coordination than dtc^-. This is consistent with the study of " Long time equilibrium " which indicates that $Cu\,(dtp)_2$ exists with further two weakly bonded dtpH groups in the axial positions in chloroform solutions.

I. INTRODUCTION

IN the past, electron spin resonance (esr) has been used to study the equilibrium between a diamagnetic inorganic compound and a paramagnetic one.[1] It has also been used to study the dynamics of solvent coordination.[2] However, not many reactions, where a paramagnetic compound is converted into another paramagnetic compound have been studied by this method. The g-tensor, A-tensor, line widths, line shapes, superhyperfine structures and the intensity of absorption observed in an esr spectrum can be used as finger prints to identify the different paramagnetic products of a reaction and to determine their concentrations. Sometimes it is possible to use the reaction data of the paramagnetic compounds to study the competing reactions of diamagnetic compounds present in the reaction mixtures.

Our attempts to study the reaction of cupric diethyldithiocarbamate (having the molecular formula $Cu[(C_2H_5)_2 NCS_2]_2$ and denoted as $Cu(dtc)_2$) with diethyldithiophosphoric acid [having the molecular formula $(C_2H_5O)_2 PS_2H$ and denoted as dtpH] using esr have yielded not only the thermodynamic constants of the reactions, but also interesting structural information.

II. MATERIALS AND TECHNIQUES

Sodium diethyldithiocarbamate was prepared by the reaction of NaOH, CS_2 and diethylamine in aqueous medium at about 7° C. This was purified by crystallisation. $Cu(dtc)_2$ was prepared in an aqueous medium by adding cupric chloride to the solution of sodium diethyldithiocarbamate. The cupric complex $Cu(dtc)_2$ was obtained as a precipitate. This was purified by recrystallising from chloroform several times. Diethyldithophosphoric acid (dtpH) was prepared from the reaction of phosphorus pentasulfide with a slight excess of ethanol in dry nitrogen atmosphere.[3,4] The ethanol used had been dried, degassed and saturated with nitrogen prior to the reaction. The purity of the compounds were checked by elemental analysis for carbon and hydrogen and by nuclear magnetic resonance. For additional check, solutions of dtpH in excess ethanol were also used in some experiments. In these cases, the concentration of dtpH was estimated by assuming 100% conversion of P_2S_5 into dtpH by its reaction with ethanol.[4] Solutions of $Cu(dtp)_2$ were obtained by treating the solutions of dtpH with cupric chloride. The mixed complex cupric diethyldithiocarbamate-diethyldithiophosphate, $Cu(dtc)(dtp)$, was prepared from the reaction of dtpH and $Cu(dtc)_2$ in 2:1 molar proportion in chloroform solutions and allowing the reaction to con-

tinue for 48 hours. The esr spectra of these solutions showed that the yield of Cu (dtc) (dtp) was about 80%.

Chloroform (B.D.H. Analar) was used as the solvent to carry out the ligand exchange reactions, as all the reactants and products of the reaction were soluble in it. Reaction mixtures in chloroform were prepared for different values of Y and p, where Y is the initial molar concentration of Cu (dtc)$_2$, (Y is also the sum of molar concentrations of cupric complexes present at any time in the reaction mixtures) and p = (initial molar concentration of dtpH/Y). Most of the reactions were carried out in the presence of air. Experiments were also carried out by rigorously excluding oxygen and moisture, by preparing the reaction mixtures in a dry nitrogen chamber and sealing them inside sample tubes by means of vacuum tight teflon stopcocks. The chloroform used in these experiments had been purified, dried and degassed prior to usage.

The X-band esr spectrometer used has been described previously.[5] The variable temperature studies were made using a Varian V–4540 temperature-control unit.

III. Analysis of the Spectra

If A (H), B (H), C (H),... are the line-shape functions which give the characteristic esr spectra of the paramagnetic compounds, whose concentrations are N_A, N_B, N_C, ..., the overlapped spectrum can be obtained from the function S (H), whose value at the magnetic field H_i is given by

$$S (H_i) = N_A A (H_i) + N_B B (H_i) + N_C C (H_i) + \ldots \qquad (1)$$

If we give the values of S (H_i), A (H_i), B (H_i) ... at a number of points H_i, by a least square analysis, one can determine the concentrations N_A, N_B, ... of the paramagnetic compounds present in the mixture.

The high field copper hyperfine lines were used for the purpose of analysis, as they had smaller widths compared to the other hyperfine lines. The derivative esr spectra of these high field lines for the complexes Cu (dtc)$_2$, Cu (dtc) (dtp) and Cu(dtp)$_2$ in degassed chloroform solutions are shown in Fig. 1. The spectrum of Cu (dtc) (dtp) has the spectrum of Cu (dtp)$_2$ in small concentrations. The presence of oxygen in the solutions increases the width of the esr lines. The parameters which characterise the esr spectra of these complexes were determined by matching the computer simulated spectra (assuming Lorentzian line shape) and the experimentally observed spectra

of the individual species. Different linewidth parameters had to be used for samples with and without oxygen. The parameters thus determined were used to get the line shape functions A (H_i), B (H_i) and C (H_i) in equation (1). S (H_i) were measured from the experimental spectrum leading to a determination of N_A, N_B and N_C.

$$\xrightarrow{\hspace{1.5cm}} H \xrightarrow{\hspace{1.5cm}}$$
$$20\,G$$

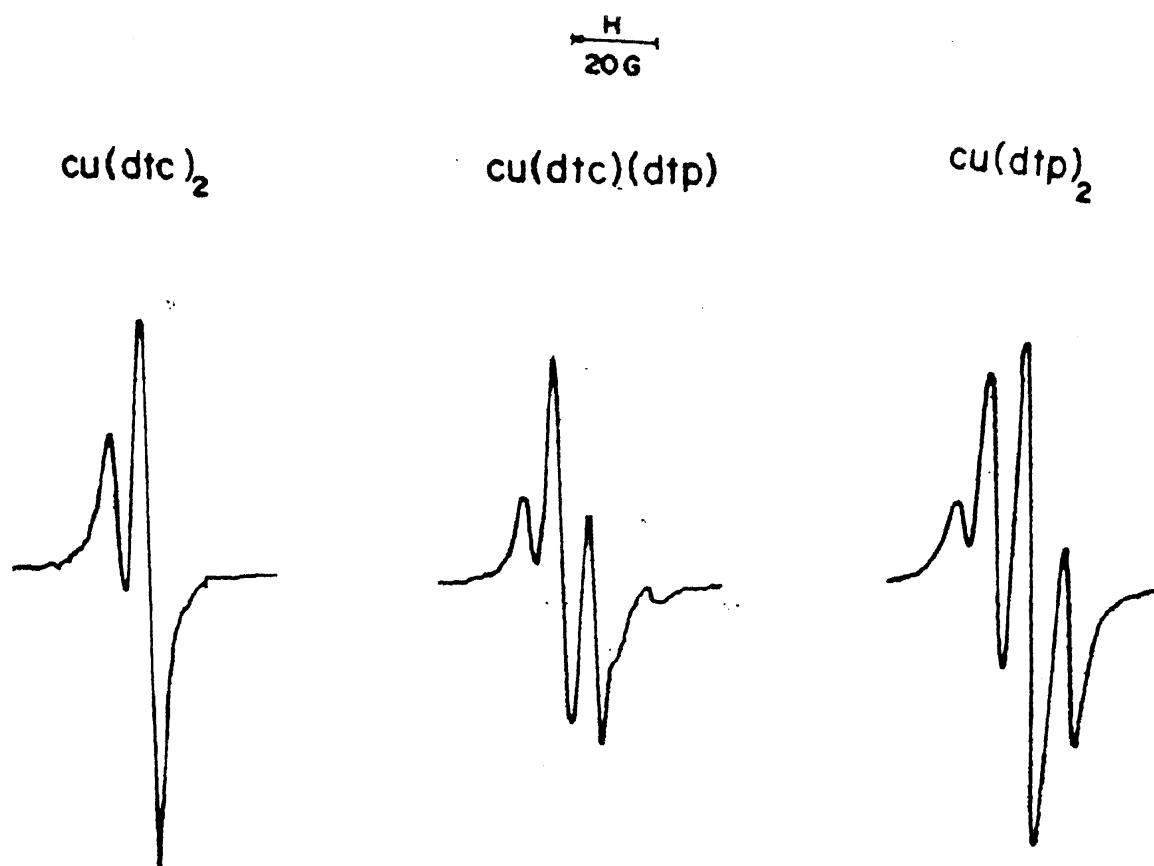cu(dtc)$_2$ cu(dtc)(dtp)   cu(dtp)$_2$

FIG. 1. The derivative esr spectra of the high field copper hyperfine lines of the complexes Cu (dtc)$_2$, Cu (dtc)(dtp) and Cu (dtp)$_2$ in degassed chloroform solutions.

IV. RESULTS

It was observed that with Y $= 0 \cdot 01$ M, the esr spectra changed with time initially. However, an equilibrium was reached in about 48 hours. This was confirmed by recording the esr spectra after waiting for another 24 hours. This equilibrium will be referred to as the " long time equilibrium", to distinguish it from the " short time equilibrium " observed in the time dependent concentration study. For reasons of convenience, the " long time equilibrium " will be discussed first.

(a) *Long time equilibrium.*—The analyses of the esr spectra from different reaction mixtures, recorded after the " long time equilibrium " was reached,
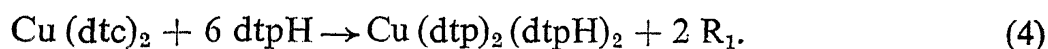
showed that the relative "long time equilibirum" concentrations of $Cu(dtc)_2$, $Cu(dtc)(dtp)$ and $Cu(dtp)_2$ were independent of the absolute concentrations but were dependent on the relative concentrations of the reactants. It was found that the reactions can be divided into two regions. For $0 < p < 2$ only $Cu(dtc)_2$ and $Cu(dtc)(dtp)$ were present in predominant concentrations. Different reaction models were tried to predict the concentrations at intermediate values of p. For the region $0 < p < 2$ the reaction,

$$Cu(dtc)_2 + 2\,dtpH \rightarrow Cu(dtc)(dtp) + R_1 \tag{2}$$
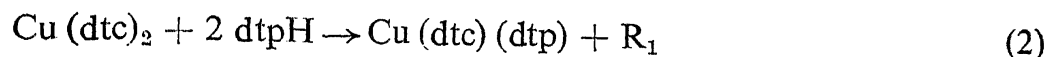
where R_1 is the reaction product of equimolar dtcH and dtpH, reproduced the observed concentrations except near $p = 2$, where $Cu(dtp)_2$ is also observed. For the region $2 < p < 6$, the reaction models, which assumed the structure of the third paramagnetic species to be $Cu(dtp)_2$, could not predict the observed equilibrium concentrations. However, the assumption that two dtpH groups are adducted to $Cu(dtp)_2$ gave excellent agreement between the experimental concentrations and those predicted from the equations:

$$Cu(dtc)(dtp) + 4\,dtpH \rightarrow Cu(dtp)_2\,(dtpH)_2 + R_1 \tag{3}$$

or

$$Cu(dtc)_2 + 6\,dtpH \rightarrow Cu(dtp)_2\,(dtpH)_2 + 2\,R_1. \tag{4}$$

Figures 2 and 3 show the experimental spectra and those predicted from reactions (2) and (4) for different values of p, in reaction mixtures prepared in the presence of air.

(*b*) *Kinetic studies and short time equilibrium.*—It has been shown above that by mixing $Cu(dtc)_2$ and dtpH in $1:2$ molar proportion one can get $Cu(dtc)(dtp)$. The yield of $Cu(dtc)(dtp)$ after 48 hours was about 80%. This enabled us to study the time dependence of reactions (2) and (3) separately. While studying reaction (3) we start with a solution presumably containing only $Cu(dtc)(dtp)$; if however $Cu(dtc)_2$ and $Cu(dtp)_2$ are present at the beginning of the kinetic study in small but in equal concentrations (the concentrations being smaller than that of dtpH to be added), a consideration of the equilibrium constants discussed later shows that one can (to a good approximation) treat the reaction mixture as though it contained only $Cu(dtc)(dtp)$ at the start. If these conditions are not obtained, one has to take into account the starting concentrations of $Cu(dtc)_2$ and $Cu(dtp)_2$ also.

There was a time lag of about two minutes between the mixing of the reactants and obtaining the "first esr spectrum". It was observed that the

features of the first esr spectra were independent of the absolute concentration Y (when dilute solutions were used) but were dependent on the relative concentrations p, of the reactants. Plotting the concentrations at different times (obtained from the analyses of the esr spectra recorded at regular intervals after mixing the reactants) and extrapolating to zero time, did not give the correct starting concentrations. The relative concentrations of the para-
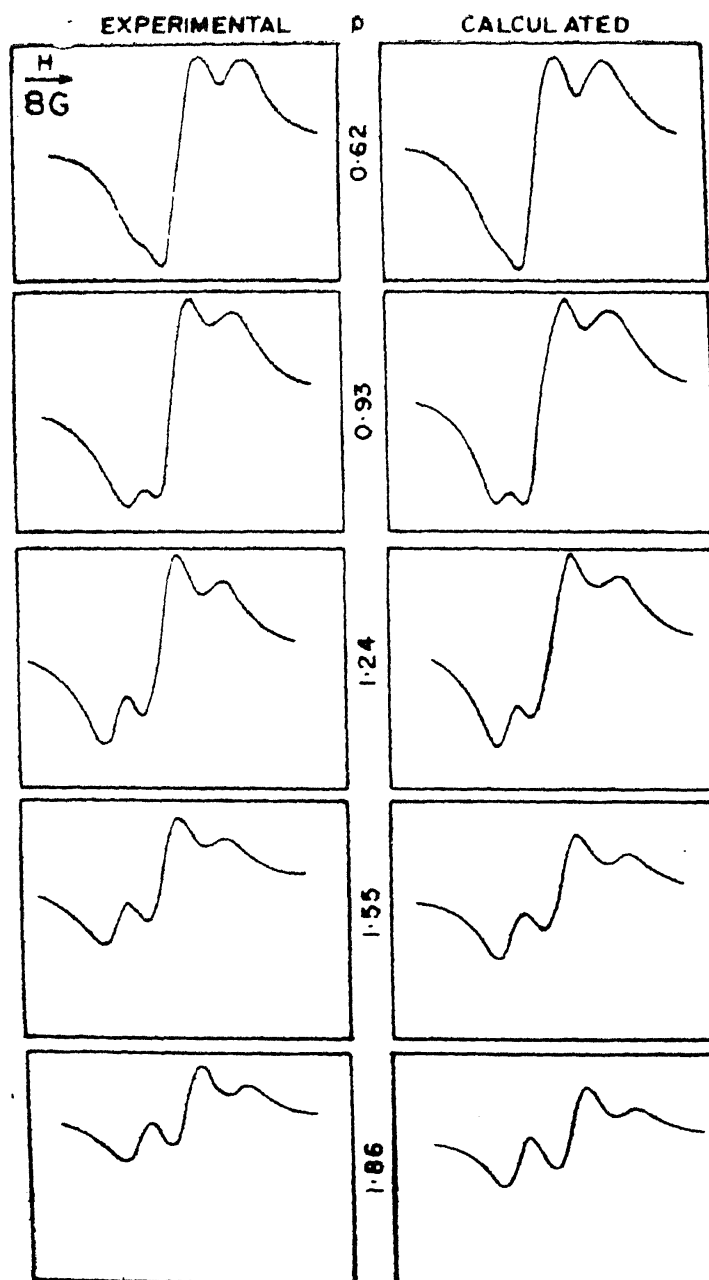

FIG. 2. Experimental and calculated esr spectra (derivative) for the reaction mixtures of Cu (dtc)$_2$ and dtpH in chloroform in the region $0 < p < 2$ after the "long time equilibrium" was reached in the presence of air according to the reaction (2).

magnetic species, obtained by extrapolation, at zero time were dependent only on p. This suggested a fast " short time equilibrium", the equilibrium being disturbed by the slow removal of one or more compounds involved in the " short time equilibrium". Since changing the temperature suddenly did not alter the esr spectra within a reasonable time, it was concluded that the enthalpy change for the reactions giving the " short time equilibrium " ⌐H ∼ 0.

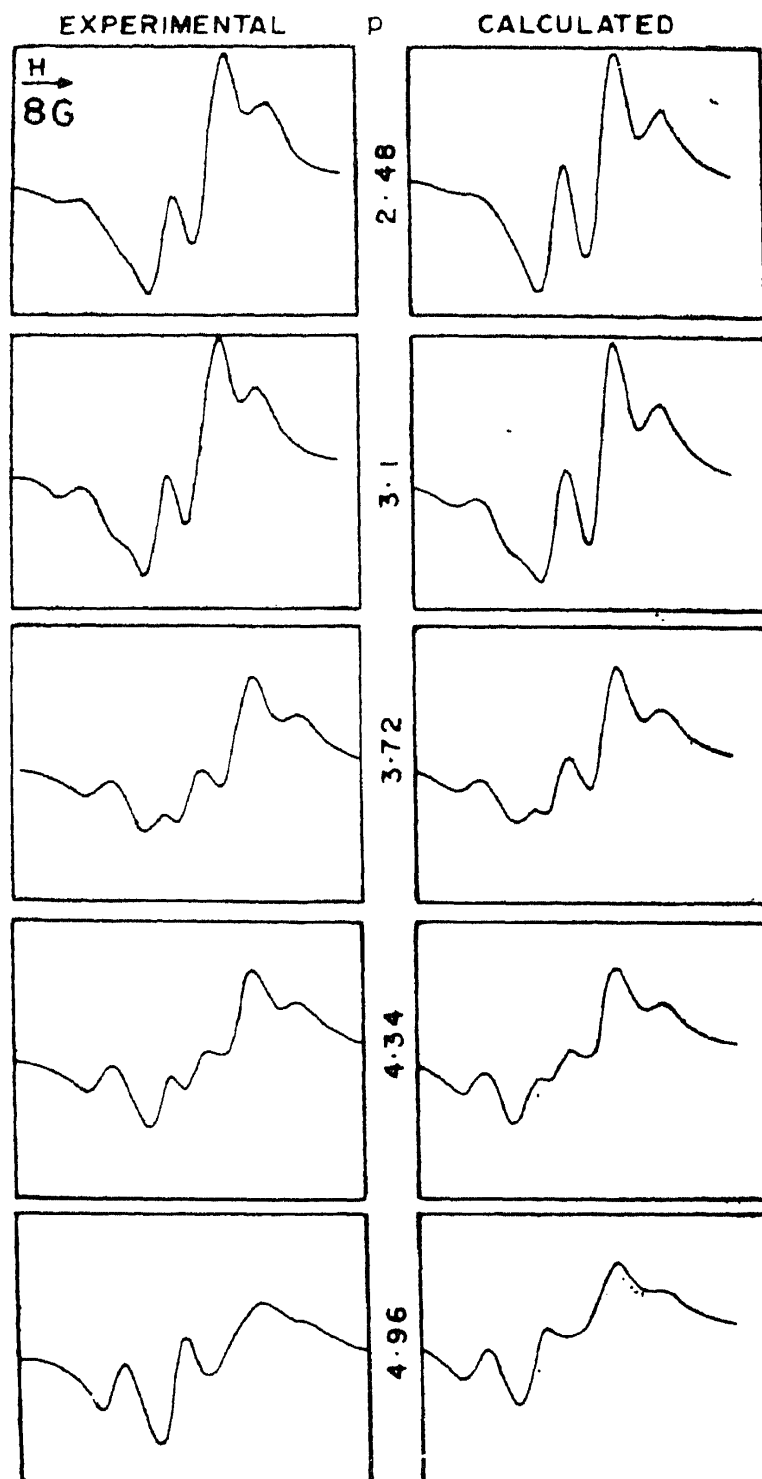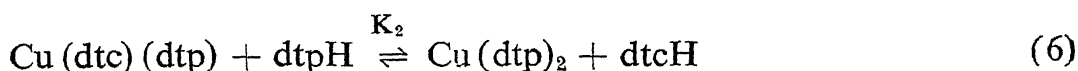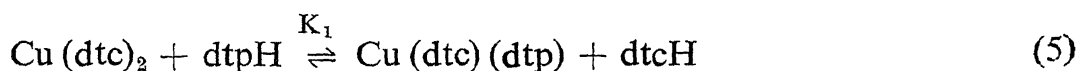FIG. 3. Experimental and calculated esr spectra (derivative) for the reaction mixtures of Cu (dtc)₂ and dtpH in chloroform in the region $2 < p < 6$ after the "long time equilibrium" was reached in the presence of air according to the reaction (4).

The reactions

$$Cu\,(dtc)_2 + dtpH \overset{K_1}{\rightleftharpoons} Cu\,(dtc)\,(dtp) + dtcH \tag{5}$$

$$Cu\,(dtc)\,(dtp) + dtpH \overset{K_2}{\rightleftharpoons} Cu\,(dtp)_2 + dtcH \tag{6}$$

where the equilibrium constants are given by

$$K_1 = \frac{[Cu\,(dtc)(dtp)]\,[dtcH]}{[Cu\,(dtc)_2]\,[dtpH]} = 0\cdot0625 \pm 0\cdot01$$

and

$$K_2 = \frac{[Cu\,(dtp)_2]\,[dtcH]}{(Cu\,(dtc)\,(dtp)]\,[dtpH]} = 0\cdot00143 \pm 0\cdot005.$$

predicted the concentrations which agreed very well with the zero time concentrations.

Since $Cu\,(dtc)\,(dtp)$ can be obtained by replacing any one dtc^- of the $Cu\,(dtc)_2$ by a dtp^- and $Cu\,(dtc)_2$ is obtained from $Cu\,(dtc)\,(dtp)$ by replacing the only dtp^- by a dtc^- one should apply statistical correction to the equilibrium constant K before equating it to exp. $(- \triangle G/RT)$ to get the free energy change in the ligand exchange reaction. Similarly, one should apply statistical correction to K_2 also. Since $\triangle H \sim 0$ for the reactions (5) and (6), we can write

$$exp.\;i\triangle S_1/R) = 0\cdot0312 \pm 0\cdot005 \;\;\text{or}\;\; \triangle S_1 = -\,7\cdot0 \pm 0\cdot3 \;\text{e.u.}$$

and

$$exp.\;(\triangle S_2/R) = 0\cdot00286 \pm 0\cdot001 \;\;\text{or}\;\; \triangle S_2 = -\,11\cdot7 \pm 0\cdot8 \;\text{e.u.}$$

for the short time equilibria (5) and (6) respectively.

The prediction of the formation of a product R_1 by the reaction of equimolar dtcH and dtpH, from the " long time equilibrium " study discussed earlier, suggests the existence of a slow reaction which disturbs the short time equilibrium with a rate constant k

$$dtcH + dtpH \overset{k}{\rightarrow} R_1. \tag{7}$$

Using the expression

$$K = \frac{x(x - R_1)}{(y - x)(pY - x - R_1)} \tag{8}$$

for the equilibrium constants K_1 and K_2 we can determine the concentration x of the cupric complex occurring on the right-hand side of equation (5) or (6), if we know (R_1). Assuming a bimolecular reaction for (7) we can write

$$\triangle [R_1] = k(x - [R_1])(pY - x - [R_1]) \triangle t \tag{9}$$

for the increase in R_1 in an interval $\triangle t$. $\triangle t$ was chosen to be small enough ($\triangle t \sim 0.01$ minute), so that the changes in the concentrations of dtcH and dtpH due to the formation of R_1 in $\triangle t$ are small compared to the concentrations of dtcH and dtpH, so that they can be treated as constants over the period $\triangle t$. Using (8) and (9) and the boundary condition $[R_1] = 0$ at $t = 0$, the concentration x, of Cu (dtc) (dtp) in reaction (5) or that of Cu (dtp)$_2$ in reaction (6), was determined as a function of time using the appropriate equilibrium constant values. The value of k was varied to get the best fit with the experimentally observed time dependence. Figures 4 and 5 show the calculated concentrations and typical observed concentrations for different values
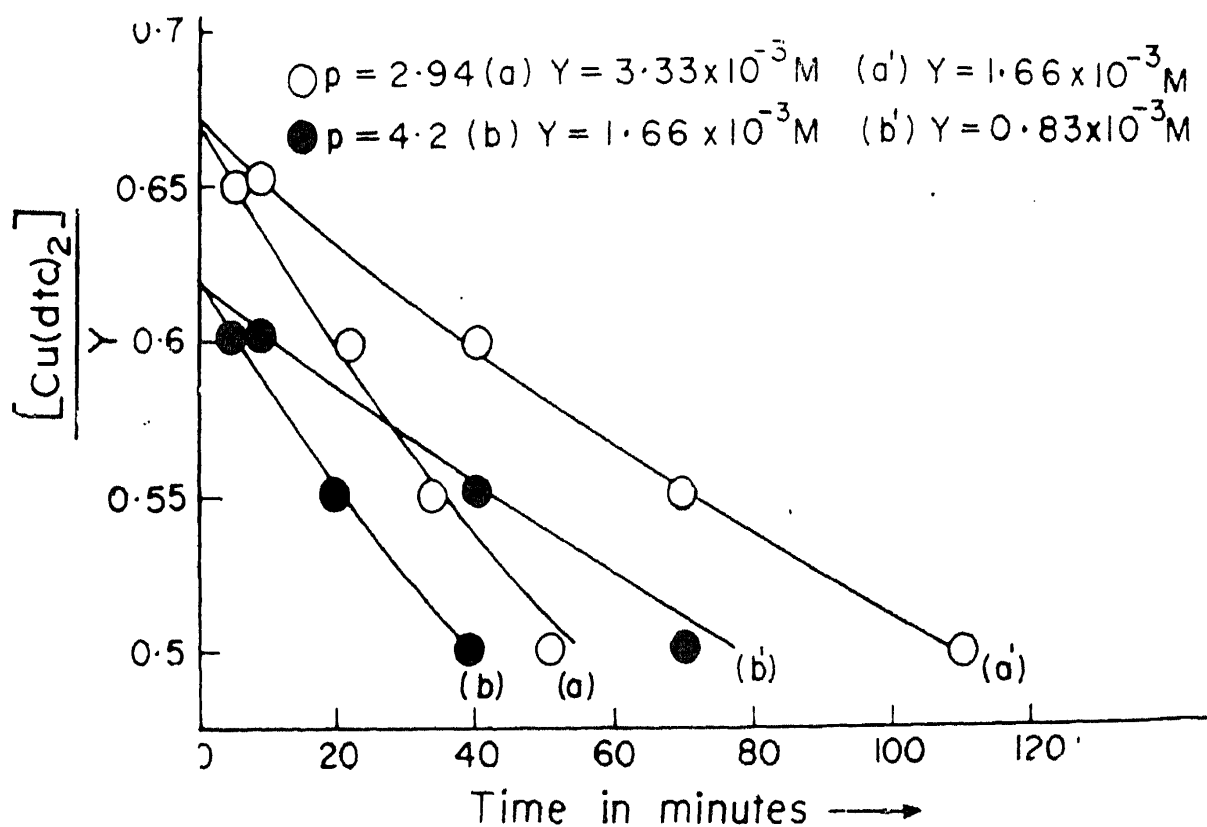

FIG. 4. Plot of $[Cu(dtc)_2]/Y$ vs. time. Points were experimentally determined from the study of reaction (2) at 26° C. Solid lines were computed using the equilibrium constant $K_1 = 0.0625$ for the equilibrium (5) and the rate constant $k = 0.07$ l.mole sec^{-1} for the reaction (7).

of p and Y as a function of time for the reactions at 26° C. Since the same reaction (7) is responsible for the time dependence of the concentrations in reactions (5) and (6), we should expect the same k to explain the time dependence in both the reactions, and it is gratifying to note that the same value of $k = 0.07$ l. $mole^{-1}sec.^{-1}$ was obtained in the two cases, for the reactions at 26° C.
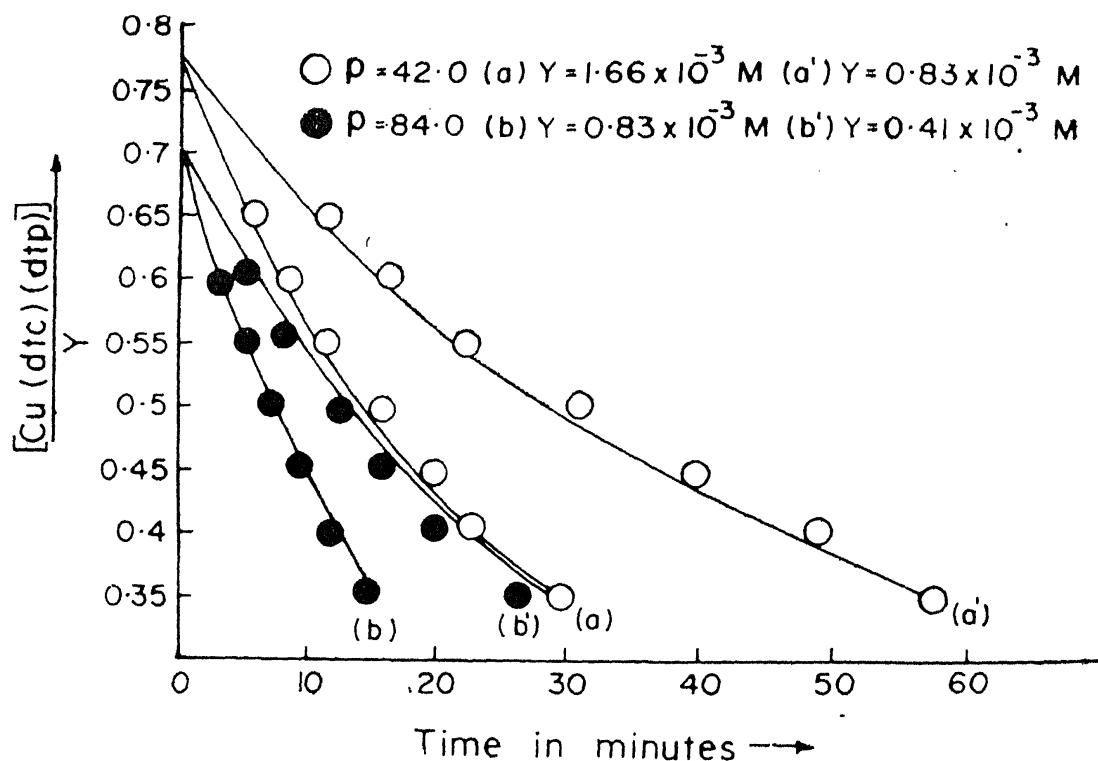

FIG. 5. Plot of [Cu dtc) (dtp)]/Y vs. time. Points were experimentally determined from the study of reaction (3) at 26° C. Solid lines were computed using the equilibrium constant $K_2 = 0.00143$ for the equilibrium (6) and the rate constant $k = 0.07$ l.mole sec^{-1} for the reaction (7).

The values of k for these reactions at temperatures between 10° C and 45° C were also obtained. Figure 6 gives the plot of $\log (k_T/k_{299})$ vs. $1/T$. The temperature dependence of the rate constant could be expressed in terms of the Arrhenius equation

$$k_T = A \exp. (- \triangle E/RT) \tag{10}$$

with $A = 10^{13.3}$ $sec.^{-1}$ and $\triangle E = 20.2$ kcal. $mole.^{-1}$ With the assumption that the transmission coefficient is unity, the values of the enthalpy of activation $\triangle H^*$ and entropy of activation $\triangle S^*$ obtained for the reaction (7) are 19.6 kcal. $mole^{-1}$ and 0.4 e.u. respectively.

The value of k obtained from chloroform solutions containing 2% ethanol v/v were within the limits of experimental error ($\sim \pm 0.02$) from those obtained for pure chloroform solutions. However, use of chloroform solutions containing 20% ethanol v/v doubled the value of the rate constant k.

(*c*) *Effect of oxygen and moisture.*—The effect of oxygen and moisture on the long time equilibria, short time equilibria and the rate constant k were studied by comparing the esr spectra of two portions of the same reaction
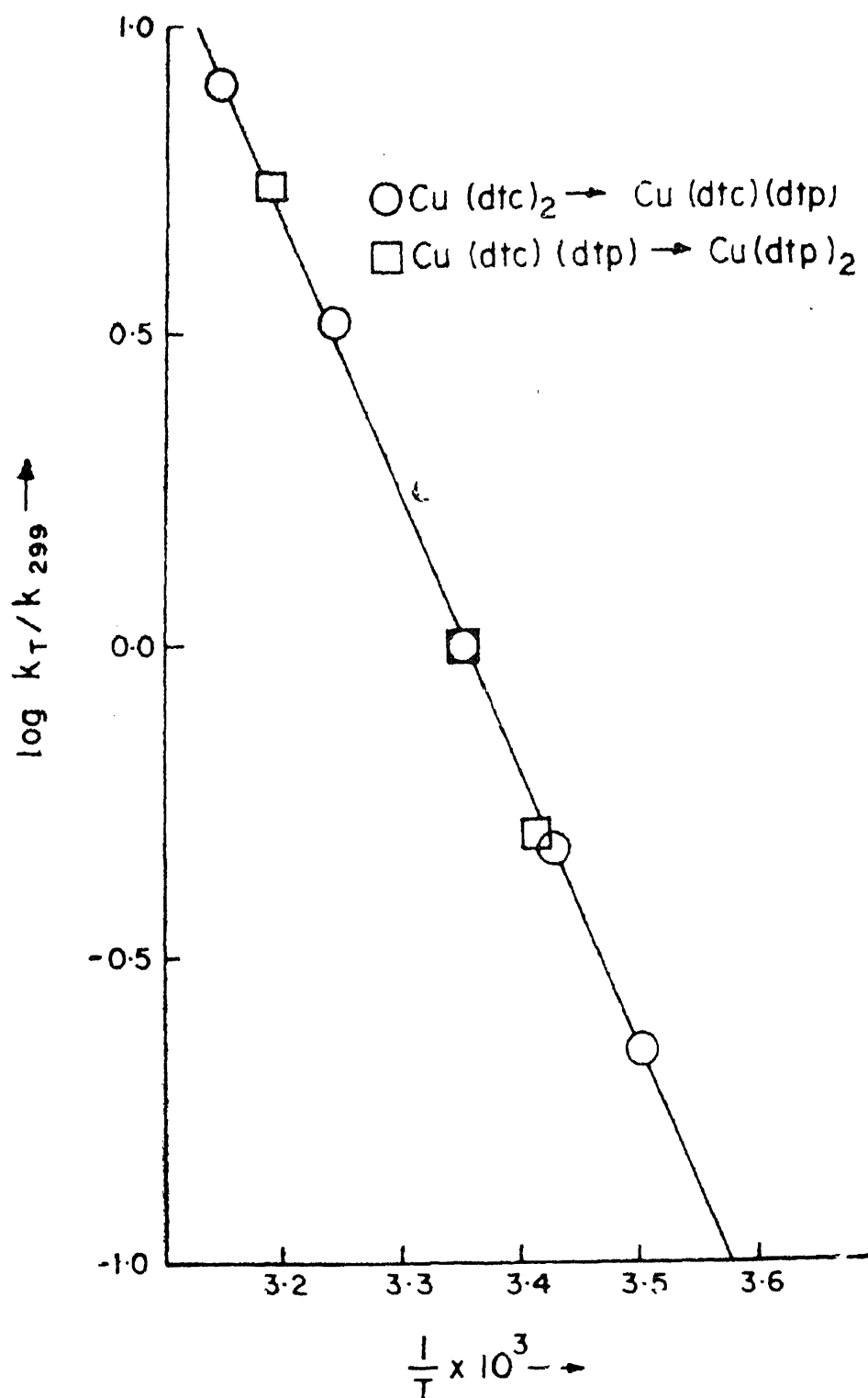

FIG. 6. Plot of log k_T/k_{299} *vs.* 1/T, where k is the rate constant for the reaction (7).

mixtures at different times, one portion sealed in dry nitrogen atmosphere and the other exposed to air. The former portion gave narrow esr lines, whereas the latter gave broader esr lines showing the presence of oxygen. However, an analysis of the two esr spectra using methods discussed earlier showed that the concentrations of the different paramagnetic species were the same in both the portions. Figure 7 shows the experimental and the computed spectra for a pair of samples compared at the same time after initiation of the reaction; the concentrations of the paramagnetic species were assumed to be the same in both the samples for computer simulation, only the line width parameters were altered to take into account broadening due to the presence of oxygen. The results on the long time equilibria, short time equilibria and the rate constant k, obtained in this set of experiments agreed well with those obtained from experiments where the reaction mixtures were prepared in the presence of air. Further confirmation of the effect of oxygen was obtained by spot checks, where the reaction in the first portion was allowed to proceed in dry nitrogen atmosphere, but the esr spectra were recorded after admitting air. The features of these spectra were the same as those obtained from the second portion (where the reaction had been allowed to proceed in the presence of air).

V. DISCUSSION

(a) *Nature of R_1.*—To investigate the possibility of R_1 being a bimolecular species (dtcH–dtpH), the nmr spectra of dtpH in solutions of carbon tetrachloride, chloroform and benzene were taken. It was observed that the position of SH proton was concentration dependent, suggesting an equilibrium between polymeric species. Molecular weights determined from the depression in freezing point were also concentration dependent. The values of the molecular weights showed that the equilibrium was predominantly between the monomeric and dimeric dtpH. It was also found that the concentration of dimers, at the concentrations used in esr experiments, were less than 10%. Since the long time equilibrium study requires 100% conversion of dtcH into R_1, R_1 being the species (dtcH–dtpH) is unlikely.

However, it is known that dtcH decomposes into $(C_2H_5)_2NH_2{}^+$ and CS_2 when it picks up a proton in acidic media.[6] The increased value of the rate constant, k, in ionising media, indicates the possibility of a charge transferred transition state, finally yielding a charge transferred compound. The reaction (7) is reminescent of the reaction[7] $(C_2H_5)_3N + CH_3I \rightarrow (C_2H_5)_3N^+ \ CH_3I^-$. All these indicate that the reaction (7) is likely to be

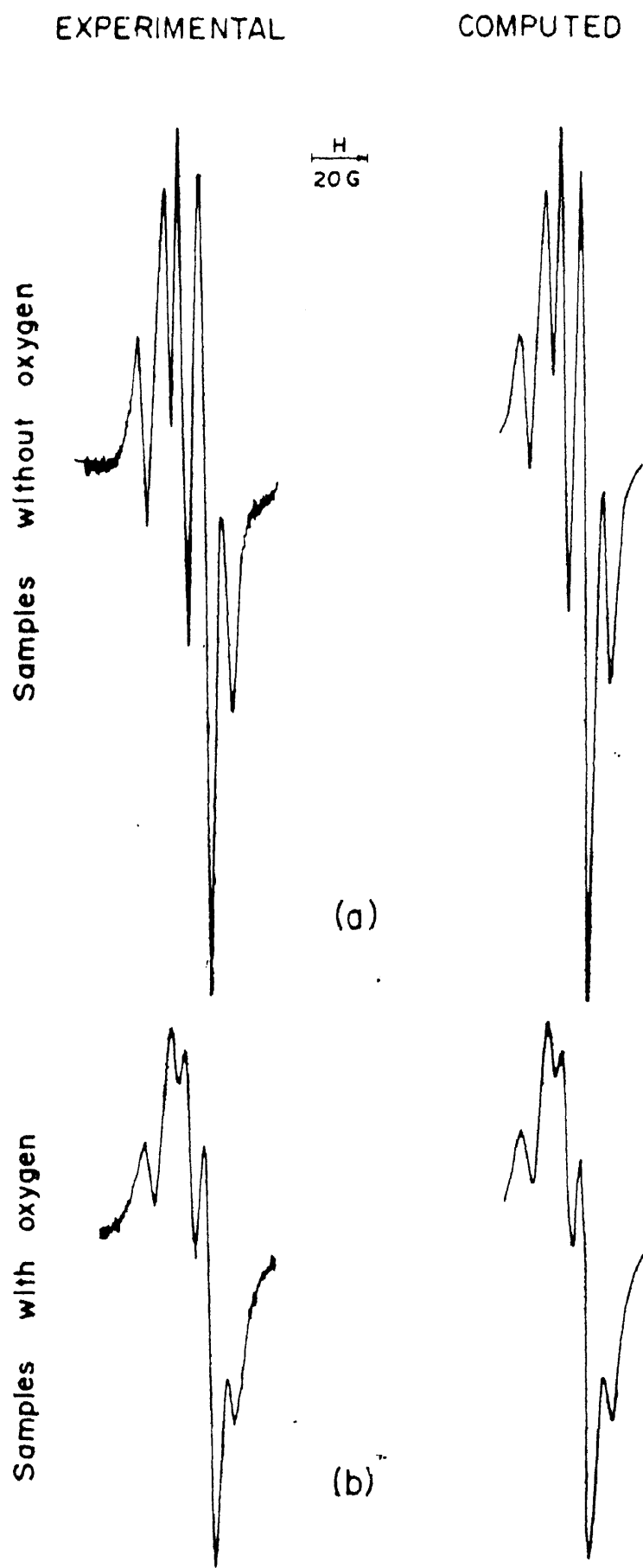$$dtcH + dtpH \xrightarrow{k} (C_2H_5)_2NH_2{}^+dtp^- + CS_2. \qquad (11)$$
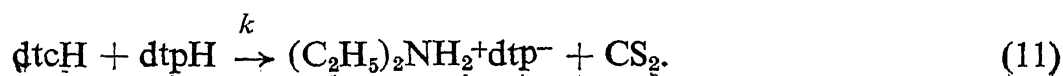
FIG. 7. The experimental and computed derivative esr spectra for pair of solutions, (a) for the solution sealed in dry nitrogen atmosphere, (b) for the solution exposed to air, while studying reaction (3). The computed spectra were obtained using the appropriate esr parameters for the two situations and concentrations [Cu (dtc) (dtp)]/Y = 0·57 and [Cu (dtp)$_2$]/Y = 0·43.

The possibility of this stable product was investigated by adding dtpH to excess of diethylamine. The solid product obtained, after evaporating the excess diethylamine, was dissolved in chloroform. The nmr spectrum Fig. 8 shows the presence of CH_2 groups of $(C_2H_5)_2NH$ (P_1) and those of dtpH (P_2) in equimolar concentrations, confirming the existence of a stable product $(C_2H_5)_2NH_2^+dtp^-$. It should be mentioned that the nmr spectra of the reaction mixtures of $Cu(dtc)_2$ and dtpH after the long time equilibrium was reached, also showed peaks corresponding to P_1 and P_2 [the peaks P_1 and P_2 were absent in solutions of $Cu(dtc)_2$] consistent with the expectations from reactions (2) and (4). However, no quantitative calculations were carried out as the lines were weak and the structures were unresolved in these spectra. Thus nmr gives supporting evidence for the formation of a stable product R_1 according to reaction (8), in the reaction (2) and (4).

$P_0 \rightarrow CH_3$ groups of $(C_2H_5)_2 NH_2^+$ and dtp^-

$P_1 \rightarrow CH_2$ group in $(C_2H_5)_2 NH_2^+$

$P_2 \rightarrow CH_2$ group in dtp^-, shows splittings from interaction with ^{31}P.
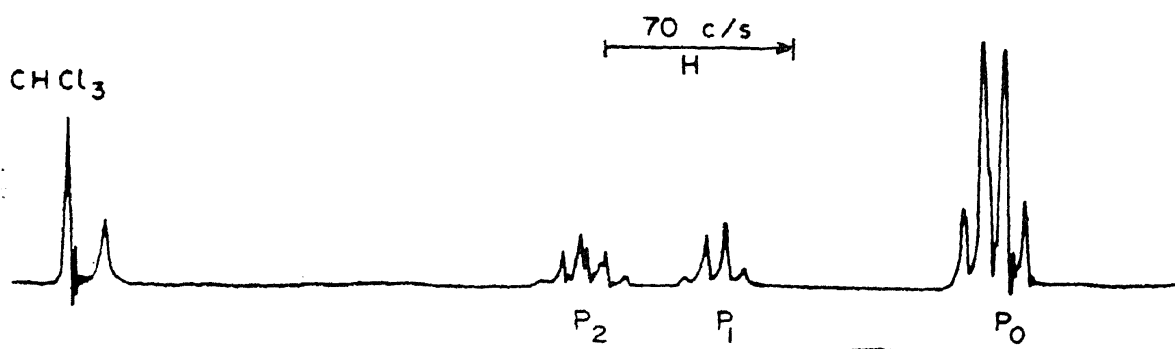
FIG. 8. Proton magnetic resonance spectrum of $(C_2H_5)_2NH_2^+dtp^-$ in chloroform.

(b) *Nature of* $Cu(dtp)_2$ *in solution.*—The " long time equilibrium study" has shown that the species of the type $Cu(dtp)_2(dtpH)_2$ are formed. It has been shown by us[8] that the g and A tensors have axial symmetry. This suggests that the two dtpH groups act as monodentate ligands bonded from axial positions (possibly through the sulphur not bonded to H and dtpH), the other two dtp^- groups acting as bidentate ligands with the sulphurs forming a square plane with Cu^{2+} in the centre. Supporting evidence for the weakly bonded dtpH groups comes from the study of nmr spectra of dtpH

solutions of suitable concentrations before and after adding cupric chloride. The formation of $Cu(dtp)_2$ results in the reduction of dtpH concentration in the solution. This should lead to a diamagnetic shift of the SH proton line, if one considers monomer-dimer equilibrium. Actually, a paramagnetic shift is observed. This can be explained if one assumes that dtpH groups can weakly bond with $Cu(dtp)_2$. There will be a fast exchange between the weakly bonded dtpH and free dtpH leading to an average paramagnetic shift of the SH proton line.

(c) *Thermodynamic parameters of short time equilibria.*—It is not surprising that the enthalpy changes in the reactions (5) and (6) are small, since in the three complexes $Cu(dtc)_2$, $Cu(dtc)(dtp)$ and $Cu(dtp)_2$, copper is bonded to four sulphurs and the covalent bonding changes only slightly from complex to complex.[8] This requires the free energy differences to come entirely from entropy differences. If one assumes that bonding with dtp^- instead of dtc^- decreases the entropy, the signs of $\triangle S_1$ and $\triangle S_2$ are explained. The differences in the entropy due to the differences in the vibrational and rotational entropy are likely to be small. It is our belief that the ligand dtp^- favours coordination with the solvent and excess ligand molecules leading to an ordered state thus decreasing the entropy. This belief is substantiated by the explanation of " long time equilibrium " concentration, which required the postulate of two dtpH groups adducted to $Cu(dtp)_2$. Though $Cu(dtc)(dtp)$ has no adducts in chloroform solutions, its esr parameters in pyridine are more affected than those of $Cu(dtc)_2$ showing higher solvent interaction[8]. Carlin and Losee[9] have also pointed out that $Ni(dtp)_2$ forms adducts with pyridine more readily than $Ni(dtc)_2$. This again confirms that dtp^- groups favour solvent coordination.

VI. ACKNOWLEDGEMENT

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