

# <sup>1</sup>H and <sup>13</sup>C NMR Study of Proton Transfer in Azoles. Mechanism of Proton Transfer in Pyrazole in Solutions Containing bis-(Acetylacetonato) Nickel(II)

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Proton Transfer, Pyrazole, Outer-Sphere Coordination

Proton transfer in pyrazole systems involving interaction with a paramagnetic transition metal complex has been studied with <sup>1</sup>H and <sup>13</sup>C NMR techniques. Kinetics of the ligand exchange in the pyrazole complex of bis-(acetylacetonato)nickel(II) has been investigated, and hyperfine coupling constants for the interaction of the nickel unpaired electron with the ligand nuclei in the complex have been determined. Catalytic admixtures of bis-(acetylacetonato)nickel(II) are shown to modify the mechanism of the proton transfer in pyrazole. The spectral data are discussed in terms of outer-sphere coordination and cooperative proton transfer effects.

## 1. Introduction

The problem of prototropic tautomerism merits interest not only because the cooperative proton transfer is of importance theoretically, but also in view of significant roles the respective reactions play in many biochemical processes responsible for membrane conductance, spontaneous and induced mutations, enzymatic reactions, etc. Though involved in quite different chemical and biochemical transformations, the proton transfer processes have obviously a very general nature, depending, probably, on the specific nature of the proton particle: on the one hand, it is heavy enough to be considered a part of the molecular skeleton and to contribute to molecular normal modes of vibration; on the other, it is essentially small to display quantum mechanical behaviour in the transfer elementary event.

## 2. Statement of the Problem

Diazoles occur in solutions as selfassociated aggregates, mainly in the form of cyclic trimeric species in the case of pyrazole and open-chain oligomers in the case of imidazole<sup>1-3</sup>. The selfassociation is due to intermolecular hydrogen bonds between the amino- and imino-functions of the neighbouring molecules. The proton transfer takes place within these H-bonds by the mechanism of prototropic rearrangement, degenerate and fast on the

NMR time scale at room temperature. Earlier, we have shown that at lower temperatures, contribution to the proton transfer kinetics from activation processes decreases while that from subbarrier tunnel penetration increases<sup>4,5</sup> as evidenced by non-linear character of the Arrhenius plot for the proton transfer rate constant and by anomalous isotopic effects<sup>4,5</sup>. Basically, the proton transfer event should be of quantum mechanical nature since de Broglie wave length corresponding to vibrational motion of proton is commensurate with the forbidden space region. Furthermore, contribution from excited states and hence from above the barrier transitions can safely be neglected in view of commonly used temperature conditions. In terms of the proton transfer elementary event theory by Dogonadze and Kuznetsov<sup>6</sup>, the activation energy arises from the motions of the system that are associated with classical degrees of freedom (such as fluctuation approach of molecules, structure diffusion, reorientation of the Debye part of polarization of polar solvents, etc.). It follows that the contribution from the proton transfer elementary event to the macrokinetics should increase as temperature decreases. Lowering of temperature removes masking effects of classical subsystem thus providing the possibility for the detection of tunneling.

Our aim has been to investigate the effect of heterocycle-to-metal coordination bonding on the proton transfer. We consider the case of  $\sigma$ -bonding of a metal at the imino-function of a ligand. One may anticipate the formation of two limiting types of complexes: (i) the imino-function may be fully blocked by a non-labile  $\sigma$ -bond which rules out the

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possibility for a prototropic rearrangement, as this is the case with the tetracarbonyliron diazole complexes we have synthesized<sup>7</sup>; type (ii) includes species that readily undergo ligand exchange reactions and where, therefore, the complex formation does not prevent the proton transfer<sup>8</sup>. Nickel(II) acetylacetonate has been used to investigate case (ii). This compound readily forms the 1:2 paramagnetic complexes with diazoles characterized by high rates of the ligand exchange<sup>9,10</sup>. We have measured temperature dependences for the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1 to 2 M pyrazole solutions in the presence of 1% bis-(acetylacetonato)nickel(II).

### 3. Experimental

All the ether solvents used were purified using alumina chromatography technique and then distilled over lithiumaluminum hydride under argon. Pyrazole was made from tetraethoxypropane and hydrazine according to<sup>23</sup> and distilled before use under argon at reduced pressure. Bis-(acetylacetonato)nickel(II) was made from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and acetylacetone and recrystallized from hexane. Samples for NMR measurements were prepared under argon.

The proton NMR spectra were obtained on a NMR-2305 instrument (made in U.S.S.R.) operated at 60 MHz. The  $^{13}\text{C}$  NMR spectra were recorded on a Bruker HX-90 spectrometer operated at 22.635 MHz. The  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts were measured from the methyl group of diethyl ether and TMS as internal reference, respectively.

### 4. Results

The results obtained in our study of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of pyrazole in tetrahydrofuran/diethyl ether solution in the presence of 1%  $\text{Ni}(\text{acac})_2$  show that the limiting low-temperature spectra are observed at much higher temperatures in this case than in the absence of paramagnetic species<sup>4</sup>.

The  $^{13}\text{C}$  NMR spectrum of pyrazole solution in THF/ $\text{Et}_2\text{O}$  in the presence of 1%  $\text{Ni}(\text{acac})_2$  consists of three signals at  $-90^\circ\text{C}$  (Fig. 1). The two lower-field resonances arise from  $\text{C}^{3,5}$  nuclei, whereas the  $\text{C}^4$  signal is shifted upfields. The  $\text{C}^{3,5}$  lines broaden with temperature and coalesce at  $-40^\circ\text{C}$ . Within these temperature limits, the contribution to the  $\text{C}^{3,5}$  line width due to periodical occurrence of the molecule within the metal coordination sphere (the factor fully responsible for the  $\text{C}^4$  line width) is negli-

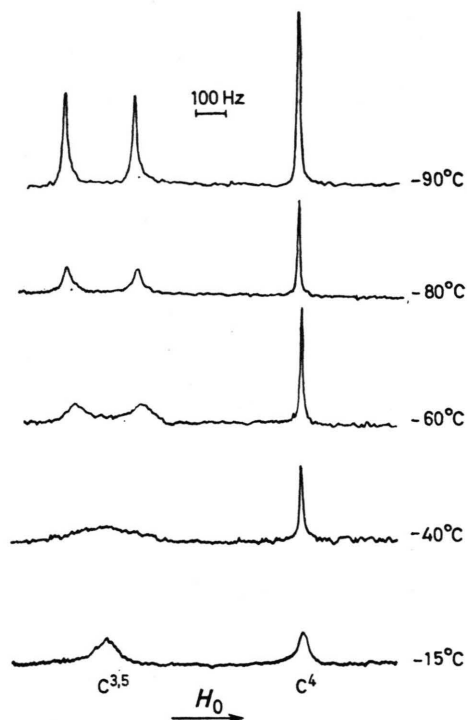


Fig. 1.  $^{13}\text{C}\{^1\text{H}\}$  spectra of pyrazole at various temperatures.

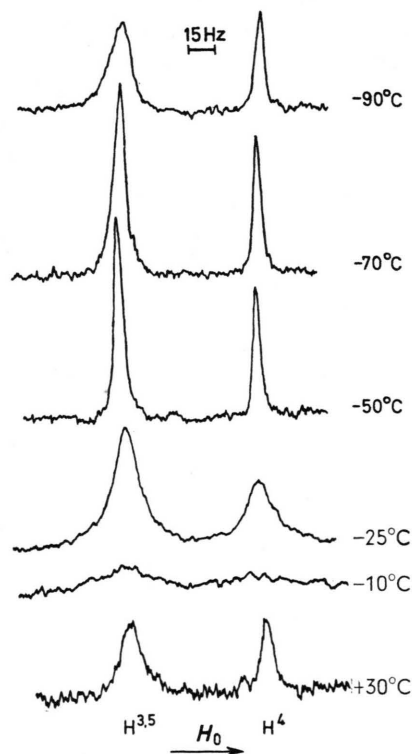


Fig. 2.  $^1\text{H}$  NMR spectra of pyrazole aromatic protons at various temperatures.

gibly small compared with "tautomerism" broadening. No effect of prototropic tautomerism is detectable in the proton NMR spectra (Fig. 2) since the high rate of the proton transfer results in averaging the spectra of the tautomers. The temperature dependence of line broadening caused by the ligand exchange between the medium and the coordination sphere of the paramagnetic ion is shown in Figs 3 and 4. Another spectral parameter, the chemical

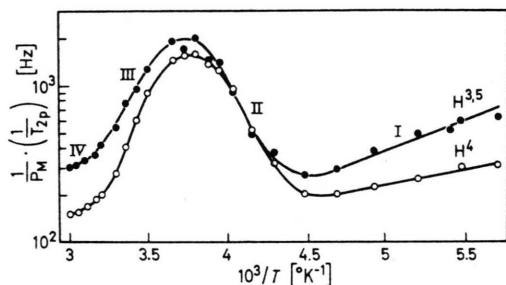


Fig. 3. Temperature dependence of line broadening for resonances from aromatic protons.

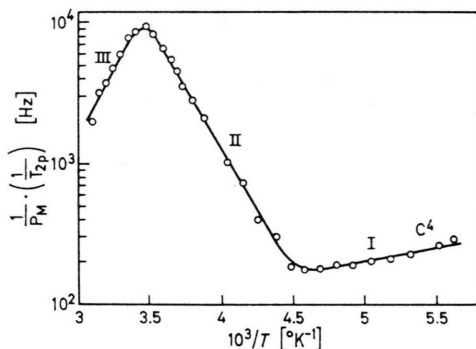


Fig. 4. Temperature dependence of  $\text{C}^4$  resonance line broadening.

shift value, is also temperature dependent. Figs 5 and 6 illustrate the chemical shift *vs* temperature dependences for different positions in the pyrazole ring. The information in Figs 3 to 6 clearly demonstrates that temperature dependence of line widths and chemical shift values is characteristic of resonances from the nuclei of bases in the presence of nickel(II) paramagnetic complexes.

Swift and Connick have solved modified Bloch equations describing nuclear magnetization to obtain the following expressions for the line width and chemical shift increments depending on periodical occurrence of the molecule within a paramag-

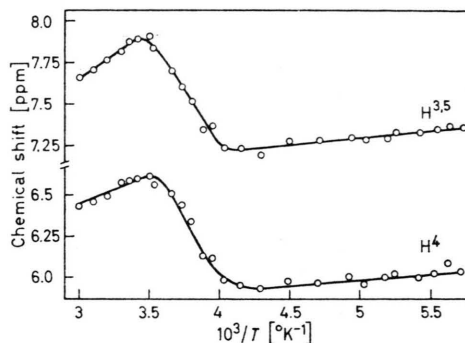


Fig. 5. Chemical shift *vs* reverse temperature dependence for pyrazole aromatic protons.

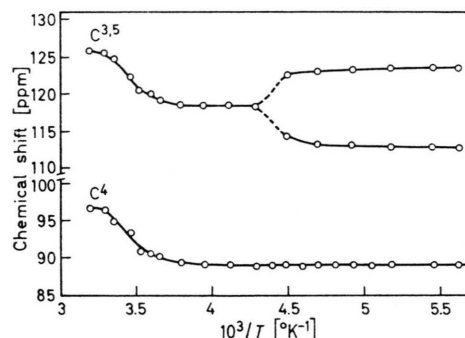


Fig. 6. Chemical shift *vs* reverse temperature dependence for pyrazole carbon nuclei.

netic ion coordination sphere<sup>11</sup>:

$$\frac{1}{T_{2p}} = \frac{P_M}{\tau_M} \cdot \frac{T_{2M}^{-2} + (T_{2M} \cdot \tau_M)^{-1} + \Delta\omega_M^2}{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2} \quad (4)$$

$$\Delta\omega_p = - \frac{P_M \cdot \Delta\omega_M}{(\tau_M/T_{2M} + 1)^2 + (\tau_M \cdot \Delta\omega_M)^2} \quad (5)$$

where all the symbols have their usual meaning:  $\tau_M$  stands for the residence time of a given nucleus within the coordination sphere,  $T_{2M}$  is the time of nuclear spin-spin relaxation in the paramagnetic state,  $\Delta\omega_M$  is the difference between the resonance frequencies of a given nucleus within the paramagnetic coordination sphere and in the free ligand, and  $P_M$  is the molar ratio of complexed molecules. The ligand exchange processes may influence the experimental parameters by different mechanisms, involving a decrease of the residence time for a nucleus in a given magnetic environment due to the chemical exchange, the difference in the precession frequencies between coordinated and free species, relaxation in the field of the unpaired electron. Any of these can become predominant depending on the

temperature. This allows to simplify expressions (4) and (5) and thus to determine the chemical exchange characteristics and parameters of coupling between the unpaired electron and the ligand nuclei from the experimental data <sup>12, 13</sup>.

In the special case that the exchange involving the inner coordination sphere of the metal is slow (low temperatures) and  $\tau_M^{-2} \ll T_{2M}^{-2}$ ,  $\Delta\omega_M^2$ , the exchange rate has no pronounced effect on resonances from free molecules, and the observed spectrum can be explained in terms of the effects of the next nearest environment (for more detail, see below):

$$1/T_{2p} = 0; \quad (6)$$

$$\Delta\omega_p = 0. \quad (7)$$

These expressions apply in region I (Figs 3, 4). The  $\tau_M^{-1}$  value increases with temperature which results in a related increase of the corresponding contribution to the line width:

$$1/T_{2p} = P_M/\tau_M. \quad (8)$$

In this case (temperature range II), two different expressions for  $\Delta\omega_p$  can be written depending on the relation between  $T_{2M}^{-1}$  and  $\Delta\omega$ :

$$\Delta\omega_p = -P_M \Delta\omega_M^{-1} \tau_M^{-2} \quad \text{for } \Delta\omega_M^2 \gg T_{2M}^{-2}, \tau_M^{-2}; \quad (9a)$$

$$\Delta\omega_p = -P_M \Delta\omega_M T_{2M}^{+2} \tau_M^{-2} \quad \text{for } T_{2M}^{-2} \gg \Delta\omega_M^2, \tau_M^{-2}. \quad (9b)$$

A further increase of temperature (region III) gives rise to rapid exchange, with  $\tau_M^{-2} \gg \Delta\omega_M^2 \gg (T_{2M} \cdot \tau_M)^{-1}$ . An exchange line narrowing occurs in this case:

$$1/T_{2p} = P_M \tau_M \Delta\omega_M^2; \quad (10)$$

$$\Delta\omega_p = -P_M \cdot \Delta\omega_M. \quad (11)$$

The temperature range of ultrafast exchange (region IV) is characterized by the relations  $\tau_M^{-2} \gg (T_{2M} \cdot \tau_M)^{-1} \gg \Delta\omega_M^2$ . Here a line broadening depends on small variations in  $T_{2M}^{-1}$ :

$$1/T_{2p} = P_M/T_{2M}. \quad (12)$$

Expression (11) still holds for the chemical shift value. Region IV is absent from Fig. 4 since the conditions of ultrafast exchange of  $^{13}\text{C}$  nuclei have not been realized in our experiment.

Thus, the plots in Fig. 3 can be used to determine the kinetics of the exchange processes involving ligand molecules bound to a complex, and the parameters of magnetic coupling between the ligand protons and the unpaired electron in the complex.

Using linear approximation for region II and drawing a line tangent to curve IV yields:

$$\tau_M = 10^{-11} \exp(8000/RT) \text{ sec}; \quad (13)$$

$$(T_{2M})_{H^{3.5}} = 1.35 \cdot 10^{-2} \exp(-930/RT) \text{ sec};$$

$$(T_{2M})_{H^4} = 2.7 \cdot 10^{-2} \exp(-930/RT) \text{ sec}. \quad (14)$$

where  $R$  is gas constant in  $\text{cal}/^\circ\text{K mol}$  and  $T$  is temperature in  $^\circ\text{K}$ . The values  $(T_{2M})_i$  only vary slightly with temperature which implies that the process determining the correlation time of nucleus-electron spin-spin coupling (the activation energy  $E_{aM} = 930 \text{ cal/mol}$ ) shows weak dependence on temperature. The nature of the rate limiting relaxation process, however, remains uncertain. We can not discriminate between the electron spin-lattice relaxation and reorientation of the complex mechanisms from our experiment, but this is not very essential for the further discussion. Using expression (13) for  $\tau_M$ , we have calculated the  $\Delta\omega_M$  values for different positions in the pyrazole ring from the data shown in Figs 3, 4 (region III) according to Eqn (10). It is known that the  $\Delta\omega_M$  vs  $1/T$  dependence is linear <sup>14</sup>:

$$\Delta\omega_M = -a \cdot \frac{\hbar \omega_0 \gamma_e}{\gamma_N} \cdot \frac{S(S+1)}{3kT}. \quad (15)$$

Here  $\omega_0$  stands for operation frequency, "a" is the hyperfine coupling constant value,  $\gamma_N$  and  $\gamma_e$  are the gyromagnetic ratios for the nucleus and the electron, respectively, "k" is Boltzman constant, and "S" is summary electron spin. The constants of spin-spin coupling involving the unpaired electron and various nuclei of the ligand have been calculated using expression (15). The values so obtained agree with the experimental chemical shifts given in Figs 5 and 6. The coupling constant values are the following:  $a_{H^4} = 2.90 \times 10^5 \text{ Hz}$ ,  $a_{H^{3.5}} = 4.52 \times 10^5 \text{ Hz}$ , and  $a_{C^4} = 5.06 \times 10^5 \text{ Hz}$  \*. It should be noted that the  $a_{H^{3.5}}$  and  $a_{C^{3.5}}$  values reflect "mixing" due to fast prototropic rearrangement and hence represent effective values.

The plots in Fig. 5 show that all the ring proton signals are shifted downfields in temperature range I where  $\Delta\omega_p = 0$ , while the positions of the  $^{13}\text{C}$

\* The temperature dependence of the  $C^3$  and  $C^5$  resonance line(s) broadening is not shown in Fig. 4. The  $C^{3.5}$  line width has been found identical with the  $C^4$  one which implies that  $a_{C^{3.5}}$  is equal to  $a_{C^4}$  to within the experimental error over temperature range III. This is unlike the situation for the  $H^4$  and  $H^{3.5}$  signals.

resonances remain strictly fixed. The reason for that is, probably, hydrogen bonding which influences magnetic environment of the carbon skeleton less strongly compared with the proton nuclei. The low temperature chemical shifts of the carbon atoms are identical with observed for systems containing no paramagnetic particles<sup>4</sup>.

Our analysis shows that the paramagnetic effects attributable to the first coordination sphere determine the nuclear relaxation kinetics at temperatures above  $-60^\circ\text{C}$ , whereas proton transfer reactions contribute to the relaxation mechanism giving rise to  $\text{H}^{3,5}$  and  $\text{C}^{3,5}$  line broadening at the lower temperatures.

The proton transfer within selfassociates as the mechanism for the  $\text{C}^{3,5}$  nuclear relaxation predominates at the lower temperatures. The Arrhenius plot of the  $^{13}\text{C}$  NMR determined lifetimes of the tautomers (which are equal to the reverse proton transfer rate constants) (Fig. 7) represents a straight line

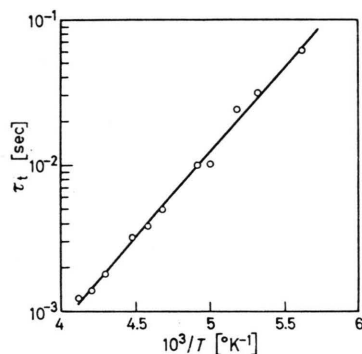


Fig. 7. Tautomer lifetime *vs* reverse temperature dependence.

in the low-temperature region, in constant to what is observed for free pyrazole which, in addition, gives much higher rate constant values<sup>4</sup>. This argues for the activation rather than tunneling nature of the proton transfer. Thus, small admixtures of bis-(acetylacetonato)nickel(II), although do not prevent proton transfer in pyrazole systems, modify significantly the proton transfer mechanism.

## 5. Discussion

### 5.1. Proton transfer model

A model aimed at the explanation of the experimental data should account for

1. proton transfer deceleration compared with free pyrazole;

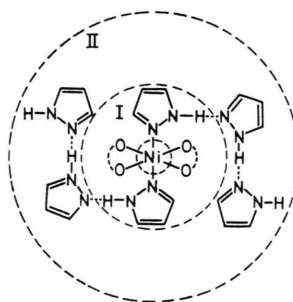
2. nonoccurrence of tunneling at low temperatures;
3. the fact that the presence of nickel acetylacetonate influences the proton transfer at the temperatures that are too low for the ligand exchange involving the first coordination sphere to go at an appreciable rate.

Apart from that, one should bear in mind that the concentration of nickel is less than the concentration of pyrazole by a factor of  $10^2$  or more.

Since it is quite clear that the ligand exchange involving the first coordination sphere can not be responsible for the observed effects we suggest the model in which ligand exchange processes involving the second coordination sphere play a predominant role.

The trimeric cyclic form of selfassociates, apart from that it is thermodynamically favoured over other types of aggregates<sup>1-3</sup>, provides the best conditions for tunneling, thanks to nearly linear configuration of the  $\text{N}-\text{H}\dots\text{N}$  groupings. In this case, the reaction coordinate coincides actually with the direction of de-Broglie wave propagation, that is the direction of high-frequency  $\text{N}-\text{H}$  vibrations\*. In the case of bent H-bridges, motion along the reaction coordinate couples to a considerable extent with low-frequency bending vibrations which lowers the tunneling probability.

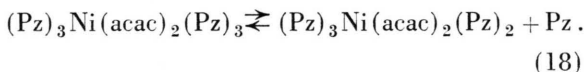
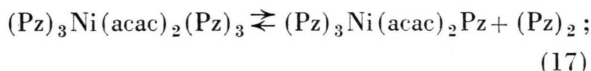
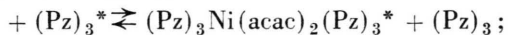
We believe that the complex formation with  $\text{Ni}(\text{acac})_2$  proceeds with opening of the selfassociate ring so that the selfassociate as a whole coordinates to the metal in the open-chain form. The first coordination sphere of the complex molecule includes species directly attached to the metal, and the second one comprises molecules bound by hydrogen bonds (Scheme I).



Two types of exchange reactions may occur in systems like shown in Scheme I: (i) exchange of the

\* In this case, we consider proton motions adiabatic with respect to motions of other nuclei<sup>6</sup>.

ligands constituting the first coordination sphere via cleavage of the Ni–N bonds and (ii) exchange of the ligands belonging to the next nearest environment with cleavage of the H-bonds:



In the first case, the selfassociated aggregate undergoes exchange as a whole [reaction (16)]. Reactions (17) and (18) exemplify the cases when the exchange transforms the outer coordination sphere, as by abstraction of dimeric (17) or monomeric (18) units; other types of the outer-sphere exchange are, of course, possible. Owing to the outer-sphere exchange processes, the system will contain self-associated species other than the equilibrium one, differing from the cyclic trimeric form both in their composition and in the geometry of H-bridges. In this case, relaxation processes leading to the formation of the equilibrium aggregates are prerequisite for operation of the proton transfer mechanism characteristic of free pyrazole. The relaxation should involve exchange of pyrazole molecules between selfassociates of different types (the formation of trimeric species), straightening of H-bridges (structure diffusion<sup>15</sup>), and cyclization. All these are activation processes. Below  $-60^\circ\text{C}$ , the first coordination sphere ligand exchange only goes at low rate [Eqn (13), Figs 3, 4], whereas the outer-sphere exchange having other activation characteristics continues to proceed sufficiently fast. This implies the occurrence of the relaxation processes leading to the equilibrium form of selfassociation in the system under consideration at temperatures below  $-60^\circ\text{C}$ . These above the barrier reactions in classical subsystem mask the elementary proton transfer event at low temperatures. The overall transfer kinetics is therefore of activation nature and tunneling becomes undetectable.

### 5.2. Outer-sphere coordination

The model we consider is based on the idea of outer-sphere coordination. It is noteworthy that system of this type are very characteristic of the coordination chemistry of diazoles. Thus, we succeeded

in synthesizing a number of diazole complexes of cyclopentadienyldicarbonyliron containing different outer-sphere ligands H-bonded at the amino function of the heterocyclic ligand<sup>17</sup>. Pyrazoles are known to form complexes of the composition  $\text{ML}_7\text{X}_2$ , where L stands for azole, M is Co or Fe, and X is anion<sup>18</sup>. Excess ligands constituting the outer coordination sphere are bound to a complex with hydrogen bridges. The plots in Figs 3 and 4 demonstrate that the  $\text{C}^4$  and  $\text{H}^4$  line widths increase slightly as temperature decreases in temperature range I where  $T_{2p}^{-1} = 0$ . A similar effect has been reported in the paper<sup>16</sup> for the proton resonances of methanol in the presence of the Co(II) and Ni(II) ions. The effect has been accounted for by long-range dipole-dipole interactions between nuclei of free molecules and unpaired electrons characterized by increase of correlation time with lowering of temperature. In the case we are discussing, the straight lines approximating  $\text{H}^4$  and  $\text{C}^4$  line broadening with reverse temperature,  $1/T$  (Figs 3 and 4, temperature range I) have slopes corresponding to activation increase of correlation time for hyperfine coupling, with activation energy of 0.93 kcal/mol. This value is identical with that found for the process governing gradual increase of the  $\text{H}^{3,5}$  and  $\text{H}^4$  line widths with lowering of temperature over temperature range IV (ultrafast exchange, Fig. 3). In temperature range I (Fig. 3), the  $\text{H}^{3,5}$  line undergoes broadening more rapidly than the  $\text{C}^4$  and  $\text{H}^4$  ones owing to a contribution from proton transfer processes which go at much lower rates in our system than in the absence of paramagnetic admixtures. More than that, at still lower temperatures, the  $\text{H}^{3,5}$  resonance splits into two components with different line widths as shown in Fig. 8. Both

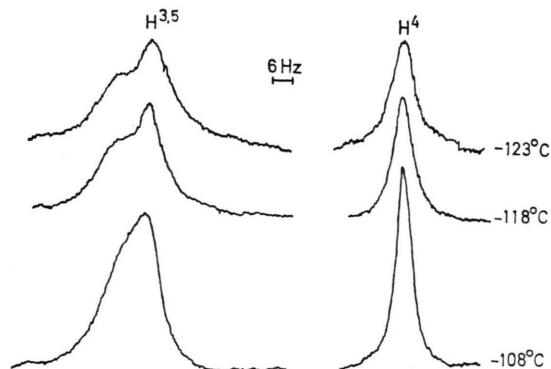


Fig. 8. Low-temperature  $^1\text{H}$  spectra of pyrazole aromatic protons.



broaden as temperature decreases similarly to the  $\text{H}^4$  line. All these findings can be rationalized within the framework of the outer-sphere coordination model. Under the conditions when the ligand exchange involving the first coordination sphere [reaction (16)] only proceeds at the rate insufficient to contribute to line widths ( $T_{2p}^{-1} = 0$ ), the outer-sphere exchange goes rapidly enough to provide for NMR-ultrafast exchange of pyrazole molecules between the medium and the next nearest environment of the metal. In this case, the relaxation mechanism for the pyrazole nuclei only depends on coupling between unpaired electrons and outer-sphere particles, in analogy to what is observed for the high-temperature exchange involving the first coordination sphere (Fig. 3, IV). Since dipole-dipole interactions are mainly responsible for the relaxation mechanism for the outer-sphere nuclei ( $r^{-6}$  potential), we observe different line widths for  $\text{H}^3$  and  $\text{H}^5$ .

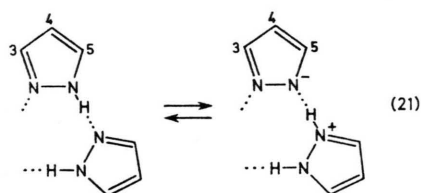
### 5.3. Relaxation of ionic structures \*

The proton transfer elementary event within an isolated intermolecular hydrogen bond gives rise to a contact ion pair. In this case, the resonances from the 3- and 5-nuclei of the pyrazole molecule, though may be temperature dependent, should be anisochronic. In fact, one can write for the chemical shift values:

$$\delta^3 = p_t \cdot \delta_t^3 + p_+ \cdot \delta_+ + p_- \cdot \delta_- \quad (19)$$

$$\delta^5 = p_t \cdot \delta_t^5 + p_+ \cdot \delta_+ + p_- \cdot \delta_- \quad (20)$$

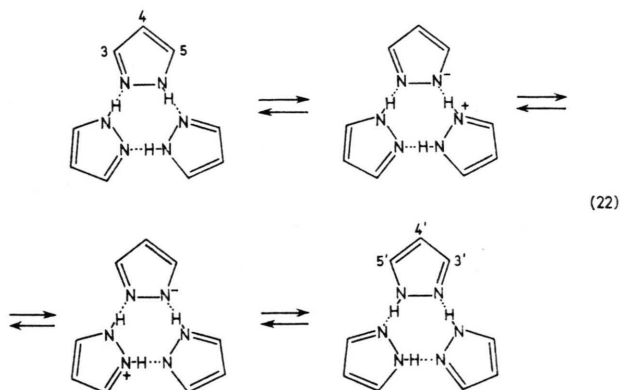
Here  $\delta_+$  and  $\delta_-$  are the chemical shift values for the cation and the anion, respectively,  $\delta_t^{3(5)}$  is the chemical shift value for a given tautomer, and  $p_+$ ,  $p_-$  and  $p_t$  stand for the respective occupancies. Ac-



cording to expressions (19) and (20),  $\delta^3 \neq \delta^5$  since  $\delta_t^3 \neq \delta_t^5$ .

\* In that we mind, the trends of the ionic structure formed by proton transfer to convert to uncharged species.

In the case of cooperative proton transfer, the positions 3,5 of the ring become isochronic:



Our experiment indicates preservation of the isochronism over a wide temperature range thus evidencing the cooperative nature of the proton transfer (22).

The idea of cooperative proton transfer (in analogy to the Grotthus scheme) has originally been put forth to account for anomalous proton mobility in water<sup>20</sup>. Further development of this idea is due to Eigen<sup>15</sup>. Latter, Zundel<sup>21</sup> has shown cooperative proton transfer to be characteristic not only of water solutions but also of all systems in general where molecules form at least two hydrogen bonds with symmetric potential. The excessive proton can undergo tunneling in such systems which results in considerable polarizability of hydrogen bonds ("superpolarizability" in Zundel terminology<sup>21</sup>) and favours dispersion-type interactions between the adjacent H-bridges<sup>21a</sup>. Finally, this results in induced proton transitions within such bonds<sup>21</sup>. The situation arise in which frequency dependence of the imaginary part of dielectric permittivity of a medium (in our case, diazole molecules also play the role of a polar medium) reaches its maximum at the frequency of proton transitions. This results in specific resonance effects responsible for cooperative proton transfer. The structures containing an excessive proton therefore prove exceedingly short-lived and we see no evidence of them as vibrational systems<sup>22</sup>.

The cyclic structure of trimeric pyrazole aggregates results in that the cooperative transfer is at the same time a relaxation mechanism for ionic structures. This mechanism, however, will not operate in open-chain structures, whether free or bound to a

complex. One may therefore expect hindering of the proton transfer in such systems.

Our discussion shows that the outer-sphere exchange processes result in violation of the selfassociation equilibrium and interfere with a usual relaxation mechanism for ionic structures. Under the conditions of the interaction with nickel acetylacetonate, a modified proton transfer mechanism should operate. Clearly, nickel(II) acetylacetonate is not the only system that can influence the proton transfer to this effect. The essential condition is a sufficiently high rate of outer-sphere exchange reactions. In fact, the outer-sphere exchange will have a pronounced effect on the proton transfer kinetics provided the lifetime of a certain pyrazole tautomer ( $\tau_t$ ) exceeds greatly the lifetime of uncoordinated ( $\tau_c$ ) and nonequilibrium ( $\tau_t'$ ) structures:

$$\tau_t > \tau_c + \tau_t' \quad (23)$$

In the case  $\tau_t' = 0$  (the system relaxes to the equilibrium selfassociation state at an essentially infinite rate), the relation

$$\tau_t > \tau_c \quad (24)$$

still holds. Hence, we can write for the rate constants:

$$k_c \cdot [\text{Ni}] > k_t \quad (25)$$

$$\text{and} \quad k_c < k_t / [\text{Ni}] \quad (26)$$

$k_c$  — is the rate of the processes (17) or (18).

These relations imply that in case the admixture concentration is by two orders less than the substrate concentration the outer-sphere exchange rate can be expected to influence the proton transfer process on the condition that the corresponding rate con-

stant is more than  $10^2$  times as great as the prototropic rearrangement rate constant. As applied to the case we are considering, this requirement is met when the exchange rate approximates the diffusion rate, which is quite realistic. In the cases when the rates of the outer-sphere exchange could have been measured, these have been found to fall in the range characteristic of diffusion processes. It follows that any reagent that can form inner and outer coordination spheres to give complexes undergoing ligand exchange reactions (*e.g.*, water and other coordination undersaturated compounds) should have a pronounced effect on the pyrazole proton transfer rate provided outer-sphere exchange proceeds at a reasonably high rate.

## 6. Conclusion

The minority of coordinating centers can seriously influence the proton transfer in pyrazoles. According to the model we suggest, no cooperative proton transfer occurs in such cases. Instead, the system behaves as comprising isolated H-bridges. It may well be that the observed effects are of the same origin as those characteristic of biochemical processes where the cooperative proton transfer plays an important role. Our experimental results and the mechanistic interpretation suggested may, we believe, aid to the understanding of regulatory activity of metals in some biochemical processes.

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