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MAGNESIUM ION MEDIATED PROTONATION OF IMINES IN ACETONITRILE

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Abstract - Addition of magnesium perchlorate to a solution of imine PhCH=N-C_4H_9 (1) and diimine PhCH=N$(CH_2)_3$N=CHPh (4), in acetonitrile, results in the formation of the corresponding iminium salts due to traces of water present in the solvent. This conclusion is based upon infrared spectra of solutions of imines, iminium salts, deuterated iminium salts and mixtures of imines and magnesium perchlorate in acetonitrile, containing varying amounts of water. The results suggest that magnesium ion catalyzed reactions of imines in CH_3CN involve iminium intermediates.

Several model studies of reduction reactions which are mediated by pyridine nucleotide linked dehydrogenases have employed metal ions as electrophilic catalysts[2,4]. The precise role of the metal ions continues to be the subject of debate[2,3]. In connection with a study of the mechanism of magnesium ion catalysis of the reduction of imines by Hantzsch ester (2,6-dimethyl-3,5-diethoxycarbonyl--1,4-dihydropyridine, an NADH model), in acetonitrile[4], it became necessary to investigate the behaviour of the imine-magnesium ion system, in that solvent.

A preliminary ^1H NMR study of mixtures of imines of type 1 and $Mg(ClO_4)_2$, in acetonitrile, indicated that displacements of chemical shifts of imine protons (HC=N-) are not correlatable with equilibria between the free imines and their coordination complexes with magnesium ions[5]. These findings led us to examine the influence of trace amounts of water, present in the acetonitrile, upon mixtures of imines and magnesium perchlorate.

It has been shown by several workers[6] that even the most carefully dried acetonitrile has a water content of at least 0.2 mM/l. Measurements of ^1H NMR spectra of mixtures of imines and $Mg(ClO_4)_2$, in acetonitrile, containing various amounts of water, suggest that the following equilibria are established between magnesium ions, imines and water.

$$Mg^{2+} + nH_2O \rightleftharpoons [Mg(H_2O)_n]^{2+}$$

$$[Mg(H_2O)_n]^{2+} + \rangle C{=}N- \rightleftharpoons \rangle \overset{+}{C}{-}NH- + [Mg(H_2O)_{n-1}OH]^{+}$$

To derive support for the abovementioned equilibria, it was necessary to demonstrate the existence of the protonated imine species, in wet CH_3CN, upon addition of $Mg(ClO_4)_2$. This was done via infrared spectroscopy. The present report describes the results and conclusions of this spectroscopic study.

Experimental

The IR spectra were measured on a Nicolet 7199 B FT-IR spectrometer with a liquid nitrogen cooled MCT detector in an 0.01 cm NaCl liquid sample cell, with a resolution better than 1 cm^{-1}.

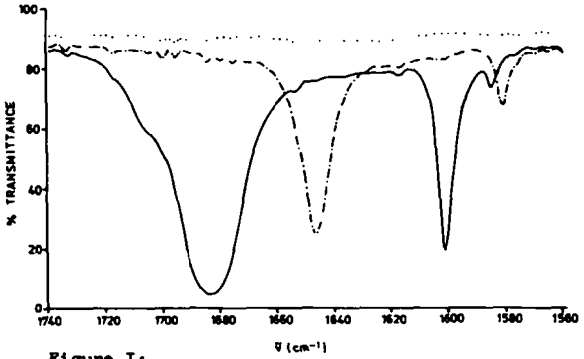

Figure I:
(a): CD_3CN (....), (b): imine 1, 0.25 M in CD_3CN (-.-.) and (c): iminium perchlorate 2, 0.25 M in CD_3CN (——).

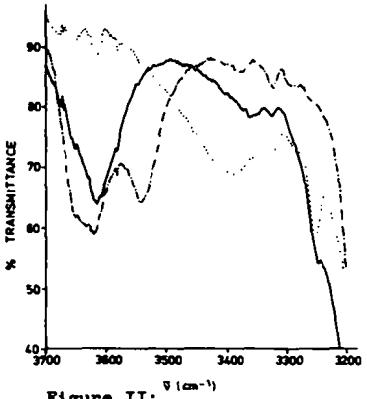

Figure II:
(a): $Mg(ClO_4)_2$, 0.25 M in CH_3CN (....), (b): H_2O, 0.1 ml/l in CH_3CN (-.-.), (c): imine 1, 0.50 M + $Mg(ClO_4)_2$, 0.25 M in CH_3CN (——).

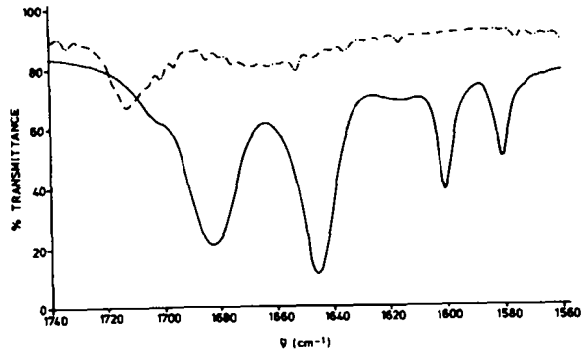

Figure III:
(a): $Mg(ClO_4)_2$, 0.25 M in CD_3CN (-.-.), (b): imine 1, 0.50 M + $Mg(ClO_4)_2$, 0.25 M in CD_3CN (——).

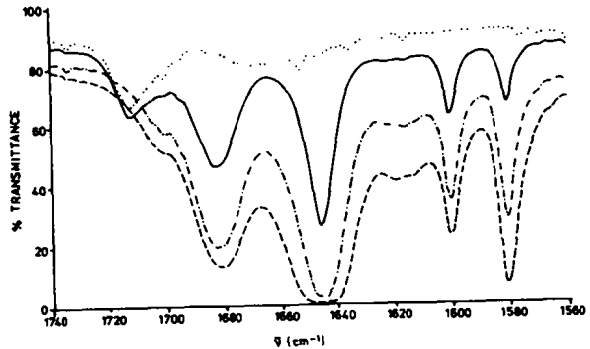

Figure IV:
(a): $Mg(ClO_4)_2$, 0.25 M in CD_3CN (....), (b): imine 1, 0.25 M + $Mg(ClO_4)_2$, 025 M in CD_3CN (——), (c): imine 1, 1.00 M + $Mg(ClO_4)_2$, 0.25 M in CD_3CN (-.-.), (d): imine 1, 2.00 M + $Mg(ClO_4)$, 0.25 M in CD_3CN (----).

Iminium salts were prepared by adding a dilute solution of the imine or diimine in anhydrous diethyl ether to a cooled (0°C) mixture consisting of an equimolar amount of perchloric acid (70% in water) and a calculated amount of acetic anhydride (for removal of water) in diethyl ether. The precipitate was filtered off, by suction, washed with anhydrous ether and dried in a heated desiccator over P_2O_5. Yields were 90 and 88% for the mono imine and diimine, respectively. The neutral imine 1 and diimine 4 were prepared according to literature procedures[4].

N-Benzylidene-1-aminobutane.$HClO_4$ (2):

Calculated for $C_{11}H_{16}NO_4Cl$: C: 50.48%; H: 6.16%; N: 5.35%; O: 24.46%; Cl: 13.55%. Found: C: 50.45%; H: 6.17%; N: 5.27%; O: 24.35%; Cl: 13.51%.

NMR (100 MHz, CD_3CN): δ 0.97 (3H, t, CH_3), 1.27-1.89 (4H, m, N-CH_2-CH_2-CH_2), 3.91 (2H, t, N-CH_2), 7.60-8.08 (5H, m, Ar-H), 8.80 (1H, s, CH=N).

N,N'-Dibenzylidene-1,3-diaminopropane.$2HClO_4$ (5):

Calculated for $C_{17}H_{20}N_2O_8Cl_2$: C: 45.25%; H: 4.47%; N: 6.21%: Cl: 15.71%. Found: C. 44.15%; H: 4.55%; N: 6.12%; Cl: 15.59%. Calculated for the bisperchlorate salt.0.62 H_2O: C: 44.15%; H: 4.63%; N: 6.06%; Cl: 15.33%.

Results and discussion

The IR-spectra of imine 1 and its perchlorate salt 2 are shown in Fig. I and their (C=N) stretching frequencies are listed in the Table.

n-BuN=CHPh (1) n-Bu$\overset{+}{N}$(H)=CHPh ClO_4^- (2) n-Bu$\overset{+}{N}$(D)=CHPh ClO_4^- (3) PhCH=N$(CH_2)_3$N=CHPh (4) PhCH=$\overset{+}{N}$H$(CH_2)_3\overset{+}{N}$H=CHPh $2ClO_4^-$ (5)

Table

compound		ν(C=N) in cm^{-1}
n-BuN=CHPh	(1)	1647
n-Bu$\overset{+}{N}$(H)=CHPh	(2)	1682
n-Bu$\overset{+}{N}$(D)=CHPh	(3)	1665
PhCH=N$(CH_2)_3$N=CHPh	(4)	1646
PhCH=$\overset{+}{N}$H$(CH_2)_3\overset{+}{N}$H=CHPh	(5)	1681

The band at 1646 cm^{-1} is attributed to the (C=N) stretching vibration (Fig. I), according to the literature[7,8]. When the spectrum of imine 1 is compared with the spectra of the protonated and deuteronated salts, 2 and 3, a displacement of the C=N band is observed from 1646 cm^{-1} to 1682 cm^{-1} (C=$\overset{+}{N}$H)[7,8] and 1665 cm^{-1} (C=$\overset{+}{N}$D), respectively. This shift in going from the protonated to the deuteronated salt is in accordance with the shift expected from the mass effect. The N-H and N-D vibrations of the perchlorates, expected in the regions 2325-2500 cm^{-1} [9] and 1800 cm^{-1}, respectively, are, unfortunately, too weak to be visible in the spectra.

Fig. II shows the 2900-3700 cm^{-1} region of the spectra of (a) a solution of $Mg(ClO_4)_2$ in acetonitrile, (b) neat acetonitrile to which water had been added, and (c) magnesium perchlorate and imine 1 dissolved in acetonitrile. The absorptions at 3629 and 3543 cm^{-1} in spectrum IIb are assignable to the antisymmetric and symmetric stretching frequencies of H_2O, respectively[10]. A band at 1632 cm^{-1} (not presented in IIb) corresponding to the bending vibration of H_2O [10], is also observed. In spectrum IIa the broad absorption around 3407 cm^{-1} is ascribed to the O-H stretching vibrations of water complexed to the magnesium ion. An analogous band is observed in the spectra of $[Mg(H_2O)_6^{++}.(ClO_4^-)_2]$[11a] and aqueous solutions of magnesium salts[11b,12]. It is noteworthy that absorptions due to free water are not present in spectrum IIa.

When imine 1 is added to the solution of $Mg(ClO_4)_2$, the absorption due to water molecules in the first coordination sphere (3407 cm^{-1}) of Mg^{2+} disappears and, in its place, a new band with a maximum at 3622 cm^{-1} appears (Fig. IIc). From the sharpness of this band and from the fact that this

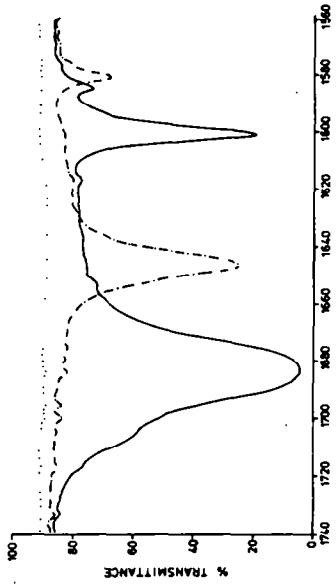

Figure VI:
(a): CD_3CN (.....), (b): diimine 4 in CD_3CN (-.-.-), (c): diimine biserchlorate 5 in CD_3CN (——).

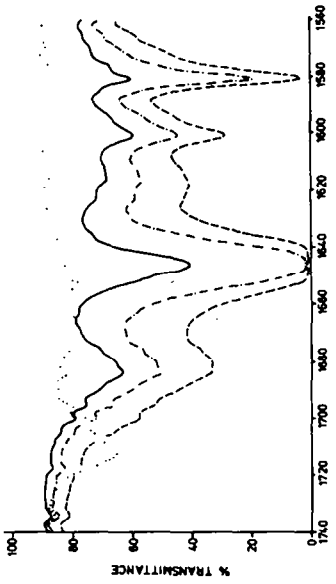

Figure VIII:
(a) $Mg(ClO_4)_2$, 0.25 M in CD_3CN (.....), (b): diimine 4, 0.12 M + $Mg(ClO_4)_2$, 0.25 M in CD_3CN (——), (c): diimine 4, 0.50 M + $Mg(ClO_4)_2$, 0.25 M in CD_3CN (-.-.-), (d): diimine 4, 1.00 M + $Mg(ClO_4)_2$, 0.25 M in CD_3CN (----).

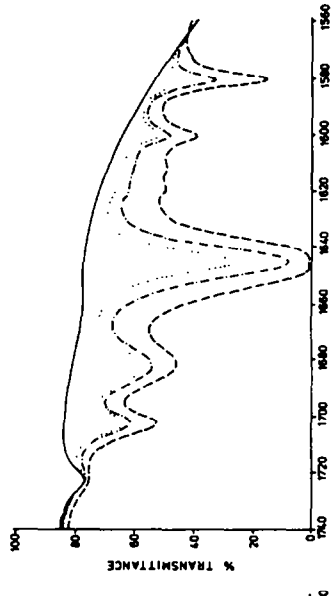

Figure V:
(a): $Mg(ClO_4)_2$ (EtOH)$_6$, 0.06 M in CH_3CN (——), (b): imine 1, 0.25 M + $Mg(ClO_4)_2$ (EtOH)$_6$, 0.06 M in CH_3CN (.....), (c): imine 1, 0.50 M + $Mg(ClO_4)_2$ (EtOH)$_6$, 0.06 M in CH_3CN (-.-.-), (d): imine 1, 0.25 M + $Mg(ClO_4)_2$ (EtOH)$_6$, 0.06 M in CH_3CN (----).

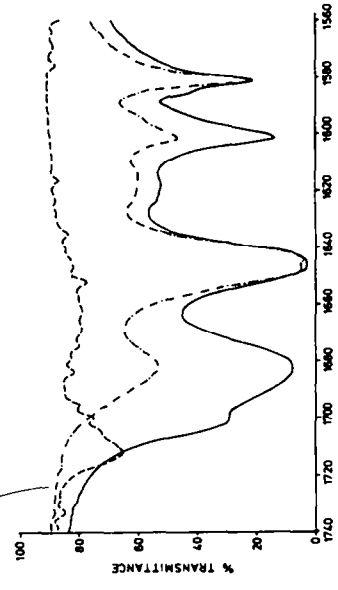

Figure VII:
(a): $Mg(ClO_4)_2$, 0.25 M in CD_3CN (1740–1560 cm^{-1}), in CH_3CN (3700–3200 cm^{-1}) (----), (b): diimine 4, 0.50 M + $Mg(ClO_4)_2$, 0.25 M in CD_3CN (1740–1560 cm^{-1}), in CH_3CN (3700–3200 cm^{-1}) (-.-.-), (c): diimine 4, 0.50 M + $Mg(ClO_4)_2$, 0.25 M + H_2O, 0.1 ml/l in CD_3CN (1740–1560 cm^{-1}), in CH_3CN (3700–3200 cm^{-1}) (——).

band is not accompanied by the appearance of absorptions at 3543 and 1632 cm^{-1} [10], it follows that the new band at 3622 cm^{-1} is not due to free water and, consequently, the imine does not displace water from the coordination sphere of Mg^{2+}. This 3622 cm^{-1} absorption band in fact comes close to that of the OH stretching vibration of NaOH (3637 cm^{-1})[13] and is tentatively assigned to this mode in $[Mg(H_2O)_{n-1}(OH)]^+$ where the value of n must be small in view of the lack of the 3407 cm^{-1} band. The latter species is formed upon donation of a proton by $Mg(H_2O)_n^{++}$ to the imine substrate. It should be pointed out that the OH stretching vibration in $Mg(OH)_2$ exhibits an absorption at 3698 cm^{-1} [14].

The 1600-1800 cm^{-1} region of spectrum III exhibits bands at 1646 and 1683 cm^{-1}, which can be assigned to ν(C=N) and ν(C=$\overset{+}{N}$H), respectively. The two bands in the region 1550-1600 cm^{-1} arise from the imine and the corresponding salt since they are also found in spectra Ib and Ic. Significantly, the spectrum contains no extra absorptions in the region 1560-1615 cm^{-1} belonging to an imine coordinated to magnesium[15].

It has been shown in the spectrum of 1 (Fig. Ib) that in the absence of $Mg(ClO_4)_2$ no iminium salt (C=NH^+) is formed. Combined with the results described above it can be concluded that magnesium ions mediate the protonation of the imine bond via the water present in the solvent acetonitrile. This was further attested by deliberately adding water to an acetonitrile solution of imine 1 and $Mg(ClO_4)_2$, whereupon the infrared spectrum of the mixture exhibited both ν(C=N) (1646 cm^{-1}) and ν(C=$\overset{+}{N}$H) (1682 cm^{-1}) whose relative intensities showed a variation ; the 1682 cm^{-1} band exhibiting an enhancement with a concommitant decrease of the 1642 cm^{-1} absorption. When, in the aforementioned experiment water was replaced by deuterium oxide, the C=$\overset{+}{N}$D band at 1665 cm^{-1} appeared, as expected.

We have searched for the presence of complexes arising from coordination of the imine to magnesium ions. In one experiment, a solution of 1 plus $Mg(ClO_4)_2$, in CD_3CN, was titrated with the imine (1). Infrared spectra of the resulting solutions are presented in Fig. IV. Inspection of the spectra fails to reveal a new absorption in the region (1560-1651 cm^{-1}) where ν(C=N) of the metal complexed imine is expected[15].In a second experiment, $Mg(ClO_4)_2$ was replaced by $Mg(EtOH)_6(ClO_4)_2$, which has been shown to form a 1:2 complex with 2-benzoylpyridine[16]. Once again, spectra of a solution containing increasing amounts of imine 1 (Fig. V) showed no absorption which could be attributed to a direct coordination of the imine to the magnesium cation. An interesting observation in Fig. V is the decrease in the absorption at 3350 cm^{-1} upon increase in imine concentration (Va ⟶ Vb ⟶ Vc-Vd). Since free ethanol absorbs at 3531 cm^{-1} [17], the broad absorption at 3350 cm^{-1} is assigned to ν(OH) of ethanol coordinated to magnesium ions. Its decrease can be rationalized in terms of partial deprotonation of the hexakisethanol complex. The ethanol within the coordination sphere of Mg^{2+} acts as a Brønsted acid towards the imine in the polar acetonitrile[18]. This conclusion[18] is supported by the presence of a relatively weak but significant absorption at 1683 cm^{-1}.

In an extension of the present study the influence of magnesium ions on diimine 4 was examined. Since 4 may be expected to coordinate with Mg^{2+} in view of its bidentate character, it was hoped that infrared spectral studies might lead to information on an imine-magnesium ion interaction. Spectra of diimine 4 and the corresponding bis perchlorate salt 5 are shown in Fig. VI. The assignment of the bands is described in the Table. From the data it is evident that the positions of the absorption maxima of ν(C=N) (1646 cm^{-1}) and ν(C=NH) (1681 cm^{-1}) bands of the imines and the diimines are very similar.

In Fig. VII the spectra of (a) $MgClO_4)_2$ in CD_3CN, (b) diimine in the presence of $Mg(ClO_4)_2$ and (c) diimine + $Mg(ClO_4)_2$ + H_2O are presented. While the prominent absorption in the presence of $Mg(ClO_4)_2$ (Fig. VIIB) is due to ν(C=N), addition of water (Fig. VIIc) causes a distinct enhancement of the band at 1683 cm^{-1}. which has been ascribed to the C=$\overset{+}{N}$H stretching vibration. Thus, also in the case of the diimine, magnesium perchlorate mediates the protonation of the base, via the water present in the mixture. In the region 3290-3700 cm^{-1} of the spectrum, the corresponding changes for the bonded water are observable. The absorption at 3407 cm^{-1} gradually disappears, while that at

3622 cm^{-1} $[Mg(H_2O)_{n-1}(OH)]^+$ becomes prominent. From these spectra it cannot be concluded whether only one or both the C=N groups of the diimine are protonated. As the (C=N) stretching frequencies of imine and diimine are similar and of the corresponding iminium and diiminium salts are almost the same, it follows, that the imine and the iminium groups in the diimine molecule do not interact intramolecularly.

Conclusions

The spectroscopic study shows that magnesium perchlorate mediates the protonation of imines of types 1 and 4, in acetonitrile, via the water present in that solvent. The equilibrium between the imines and their corresponding iminium salts is rapidly established. Since trace amounts of water are associated with acetonitrile, these results have salient implications for the mechanisms of magnesium ion catalyzed reactions of imines in acetonitrile. The role of magnesium ions in the reduction of imines by Hantzsch ester (an NADH model), in particular, will be discussed in a forthcoming paper.

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