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Nuclear magnetic Resonance Study of the Solvent Effects on Thioacetamide

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The influence of the solvents nitromethane, acetic anhydride, dioxane, propanediol-1,2-carbonate, ethylacetate, diethylether, tetrahydrofurane, dimethylacetamide, dimethylsulfoxide and hexamethylphosphoric amide on the ^1H nmr spectra of the N–H protons in free thioacetamide and its pentacarbonylchromium complex has been studied. The chemical shifts for the coordinated thioacetamide show a fair correlation with the solvent donor numbers. The chemical shifts for the free thioacetamide reveal however, the influence of both the donor and acceptor properties of the solvents. Some deviations from the general behaviour are discussed considering possible steric interactions.

Introduction

Most information about the intra- and intermolecular interactions in amide and thioamide solutions employing nmr methods has been obtained from studies of the rotational barrier for the hindered rotation about the C–N amide bond [1–6]. The influence of solvents and solute concentration on the nmr spectra of these compounds have been investigated [1–3, 7–9]. It has been found that specific interactions, which stabilize the dipolar resonance ground state structure B of amide compounds increase the rotational barrier [2, 7, 9].

A B

The solvent effects have been attributed either to hydrogen bonding [2, 3, 7, 9] or to dipolar associations between the solvent and amide molecules [2]. From the concentration effects, which also depend on the solvent, the formation of hydrogen-bonded dimers and dipolar association between the amide molecules have been suggested [8, 9]. The multiple interactions that are possible in a solution of an amide, represented by the resonance structures A and B, cannot be analysed as a function of solvent parameters without simplifying the system. The ability of thioacetamide to form complexes at the sulfur atom (1) was used in this work to form the thioacetamide (ta) chromium complex $Cr(CO)_5ta$. This complex was then used to investigate the solvent effects on the N–H line of the nmr spectrum of thioacetamide.

Experimental

The ligand thioacetamide (ta), an Aldrich product, was recrystallized twice from an ethanol–water mixture. The carbonyl complex $Cr(CO)_5ta$ was prepared by UV irradiation techniques [11–13]: 0.66 g hexacarbonylchromium(0) dissolved in 80 ml tetrahydrofurane were irradiated by a 400 watt Hanovia lamp using medium pressure of mercury for 30 minutes. After adding 0.225 g thioacetamide, the solution was stirred for 30 minutes. The solution was then evaporated under vacuum at room temperature to remove the solvent and the unreacted $Cr(CO)_6$. The dried residue was redissolved in 60 ml benzene. The addition of 15 ml petroleum ether permitted the separation of excess thioacetamide, which was removed using a Kieselguhr column. The complex was then obtained as yellow crystals by adding 40 ml of petroleum ether and by cooling the solution in a dry ice–methanol mixture. *Anal.* Calc.: S, 12.02; Cr, 19.46. Found: S, 12.43; Cr, 19.20. IR (KBr, cm^{-1}): 3460 ms, 3345 ms, 3200 w, 2940 sh, 2680 vw, 2620 vw, 1645 vw, 1632 sh, 1605 m, 1450 w, 1393 sh, 1369 w, 1300 m, 1283 w, 1155 mw, 1075 vw, 1024 sh, 1010 w, 970 m, 948 m, 720 ms, 662 s, 640 s, 580 m, 550 w, 510 w, 470 w, 450 ms, 442 ms, 407 m (s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, sh = shoulder).

The solvents were purified by standard techniques [14] and stored in a nitrogen atmosphere over molecular sieves. Their purity was checked through their nmr spectra at highest amplitude.

The ^1H nmr measurements were made on a Varian T-60 spectrometer using 5 mm o.d. tubes at 35 °C. The chemical shifts were determined using tetramethylsilane (TMS) as internal reference.

TABLE I. Amide Protons Chemical Shifts of Thioacetamide (ta) and $Cr(CO)_5$ta in Various Solvents.

Solvent	Chemical Shifts[a], ppm		Solvent Donor Number (DN) [20]	Solvent Acceptor Number (AN) [25]
	ta	$Co(CO)_5$ta		
Nitromethane (NM)	7.73 ± 0.08	8.20 ± 0.17	2.7	20.5
Acetic anhydride (AA)	7.80 ± 0.08	8.63 ± 0.08	10.5	–
Dioxane (Dx)	7.93 ± 0.05	8.80 ± 0.12	14.8	10.8
Propanediol-1,2-carbonate (PDC)	7.88 ± 0.08	8.91 ± 0.08	15.1	18.3
Ethylacetate (Etac)	8.08 ± 0.08	9.17 ± 0.08	17.1	–
Diethyl ether (ether)	7.85 ± 0.10	9.13 ± 0.15	19.2	3.9
Tetrahydrofurane (THF)	8.28 ± 0.06	9.32 ± 0.07	20.0	8.0
Dimethylacetamide (DMA)	8.96 ± 0.08	10.47 ± 0.03	27.8	13.6
Dimethylsulphoxide (DMSO)	9.10 ± 0.08	9.83 ± 0.13	29.8	19.3
Hexamethylphosphorictriamide (HMPA)	9.75 ± 0.05	10.85 ± 0.08	38.8	10.6

[a]Measured relative to tetramethylsilane.

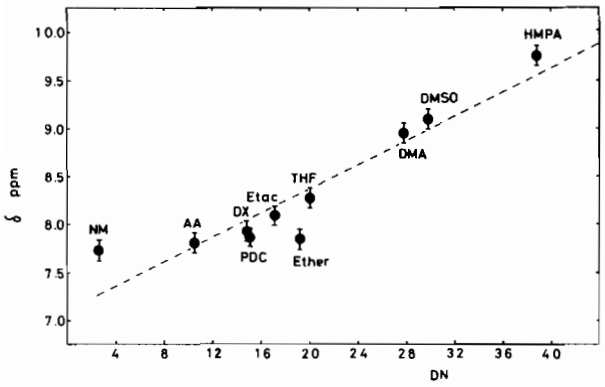


Fig. 1. Relationship between the chemical shifts of the amidic protons in thioacetamide in various solvents and the donor numbers of these solvents.

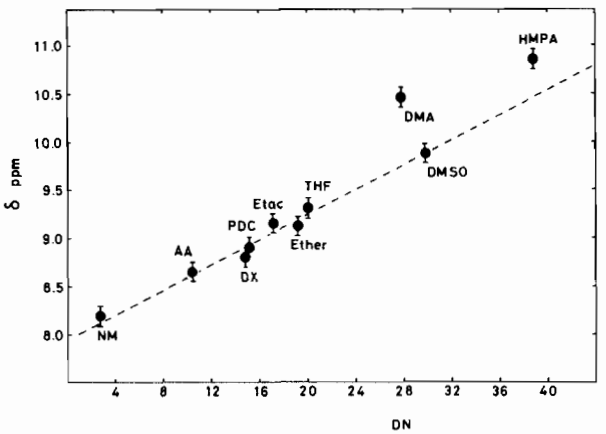


Fig. 2. Relationship between the chemical shifts of the amidic protons in the complex $Cr(CO)_5$ta in various solvents and the donor number of the solvents.

Results

The position of the nmr resonance signal of the N–H protons was measured at 35 °C in thioacetamide and thioacetamidechromiumpentacarbonyl ($Cr(CO)_5$-ta) solutions in the following solvents: nitromethane (NM), acetic anhydride (AA), dioxane (Dx), propanediol-1,2-carbonate (PDC), ethylacetate (Etac), diethyl ether (ether), tetrahydrofurane (THF), N,N-dimethylacetamide (DMA), dimethylsulfoxide (DMSO), and hexamethylphosphoric amide (HMPA).

The IR spectra of thioacetamide and its chromium carbonyl complex were compared using the band assignment made by Walter and Kubersky [15]. Through the complex formation those bands involving appreciable C=S or C–N stretching character [15] shift to lower or higher frequencies respectively. Therefore a thioacetamide sulfur atom coordination at the chromium atom in the studied complex could be inferred. A similar behaviour and coordination type has been observed for the thioacetamide complexes $Cu(ta)_4Cl$ [16], $Co(ta)_2Cl_2$ and $Ni(ta)_4X_2$ (X = Cl, Br) [17], and for N,N-dimethylthioacetamideironpentacarbonyl [18].

The chemical shifts observed using TMS as internal reference depend on the nature of the solvents as shown in Table I. The dependence of the resonance signal position on the concentration of the carbonyl complex was negligible and the deviations were within the experimental error of the determination of the resonance position. These errors were relatively large (see Table I) due to the natural signal width of the N–H protons [3]. In thioacetamide solutions only a small dependence on the concentration in solvents with low donicity was observed. No correction to infinite dilution was made and the reported values are those obtained at the lowest measured concentration.

The spectra of the solutions containing $Cr(CO)_5$ta always show besides the signal of the $Cr(CO)_5$ta the

signal due to the free ligand. Therefore there is a competition between the thioacetamide and the solvent for the same coordination site:

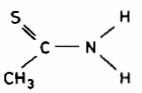
$$Cr(CO)_5ta + D\ (solvent) \rightleftharpoons Cr(CO)_5D + ta$$

The equilibrium constant for this substitution could not be calculated due to the inaccuracy of the evaluation of the resonance signal integrals. A qualitative estimate of the constants in different solvents through the signal intensities showed that they follow approximately the order NM $\gg$ DMSO > HMPA > Dx > THF $\approx$ Ether. Nonetheless the thioacetamide N–H protons chemical shifts did not show variations greater than the experimental error when adding an excess of pure ligand, so that a fast solvent ligand exchange may be neglected [19].

The chemical shifts of the thioacetamide and thioacetamidechromiumpentacarbonyl N–H protons *vs.* the donor number of the solvent (DN) [20] are shown in Fig. 1 and Fig. 2 respectively.

Discussion

The existence of different rotamers and the hindered internal rotation around the (S=C)–N bond in thioacetamides has been extensively studied by nmr spectroscopy [1–5]; the influence of the solvent, concentration and substituents on the barrier to free rotation have been attributed to the competition between the two amide bonds for electron delocalization:



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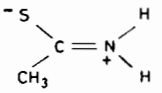


II

In order to analyse the interactions with the solvent here described, it is necessary to take into account this delocalization. According to the structure of the thioacetamide molecule, it can interact both as a Lewis acid, through the formation of hydrogen bonds, and as a Lewis base, through the sulfur atom [1]. The possibility of interaction by coordination at the nitrogen atom is not as important and can be excluded [21]. When the sulfur atom in thioacetamide is blocked by the formation of a complex, the only possible association with the solvent is through the formation of hydrogen bonds.

Although the ^1H nmr chemical shift changes produced by hydrogen bonding interactions are accompanied of a large number of other contributions, a relatively fair linear correlation between the position of the hydroxy proton chemical shifts and the enthalpy of hydrogen bonding interaction for a large number of phenol-base systems has been found [22]. It has also been found that the chemical shifts for hydroxy-protons in substituted aromatic thioacetamides, able to form intra- as well as intermolecular hydrogen bonded compounds, correlate with the phenolic $\Delta J(OH)$ frequency shifts [4]. Therefore the shifts produced by different solvents in other proton-donor solutes must be, at least in part, related with the solvent ability for hydrogen bonding interactions. The greater shifts of the amide proton resonance of the thioacetamide complex towards lower fields induced by more basic solvents, which are in general similar to those of thioacetamide solutions, show that the main interaction is a nucleophilic attack on the N–H protons. The importance of the donor strength of the solvents on the behaviour of the amidic protons in thioacetamide can be observed by using the solvent donor numbers [20] defined as proportional to the enthalpy change of the reaction,

$$D + SbCl_5 \xrightarrow{\text{1,2-dichloroethane}} D{\cdot}SbCl_5$$

$$\Delta H_{DSbCl_5} = -DN$$

The dependence of the chemical shifts of the amidic protons in thioacetamide and its chromium complex on the solvent donor numbers is shown in Fig. 1 and 2 respectively. The solvent effect on the N–H protons of $Cr(CO)_5ta$ increases with increasing solvent donicity (Fig. 2). There is a relatively fair linear relationship between the chemical shifts of the N–H protons and the donor numbers for most of the solvents. This is interpreted as the result of a solute–solvent interaction due to the nucleophilic attack of the solvent at the N–H protons. In the case of thioacetamide (Fig. 1), however, greater deviations from a linear relationship are observed.

A standard method usually used for studying the solvent influence on hydrogen bonded systems is to compare the behaviour of the X–H (X = N, O) bond strength in two related compounds, for instance, comparing the solvent shift of their frequencies ν(X–H) [23–25]. A linear correlation between the shifts indicate a similar behaviour of both compounds in each solvent, this includes all possible effects, *e.g.* hydrogen bond formation, dipolar and inductive interactions, as well as steric effects. A comparison between the chemical shifts for thioacetamide and those for the complex is shown in Fig. 3. It can be clearly seen that there is no simple relationship between both systems, and that solute–solvent interactions through the sulfur atom cannot be neglected in the thioacetamide solutions.

The effect of the coordination at the sulfur atom has been observed for amide and thioamides in protic solvents, *e.g.* water [26], formamide [27], and methanol [2], which interact with the oxygen and

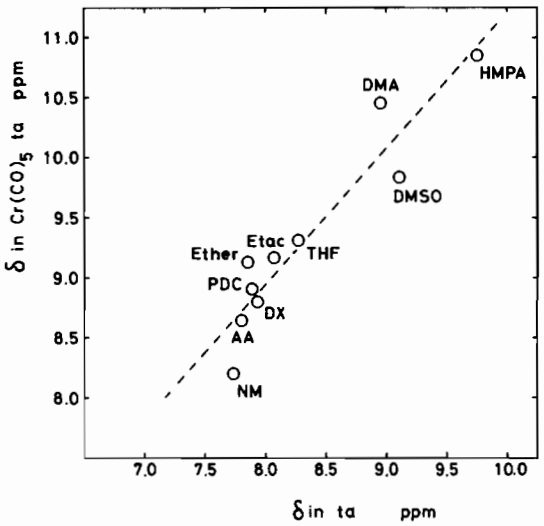
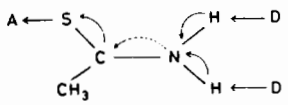


Fig. 3. Correlation between the chemical shifts of the amidic protons in the thioacetamide free and coordinated in the complex $Cr(CO)_5$ta.

sulfur atom by hydrogen bond formation. Such interaction should stabilize the polar structure II by increasing the double bond character of the C–N bond leading to higher torsional barriers.

The sequence for the dissociation constants estimated in some solvents appear also to be more influenced by the electrophilic than by the nucleophilic properties of the solvents, indicating also a solvent attack at the sulfur atom.

The cooperative effect on the N–H bond owing to a simultaneous interaction of the solvent with the thioacetamide sulfur atom as an acceptor (A) and with the amidic protons as a donor (D) can be also predicted by the bond length variation rule [28]:



The increase of the C–N bond rigidity on increasing the amidic proton–solvent interaction has been clearly observed for acetamide [29]. On the other hand, the influence of the interaction between thioacetamide and an acceptor molecule on the amidic proton resonance is reflected in the downfield shifts of the N–H resonance induced by the formation of the complex $Co(CO)_5$ta (see Table I).

The electrophilic effect of the solvent on the chemical shifts of the thioacetamide protons can be evaluated using the solvent acceptor numbers (AN) [30]. Thus, it appears to be reasonable to test a relationship such as:

$$\delta(\text{N–H}) = a\,DN + b\,f(AN) + c$$

where f(AN) stands for a function of the acceptor number, providing a solvent acceptor parameter

TABLE II. Experimental and Calculated[a] Chemical Shifts for the Thioacetamide Amide Protons.

Solvent	Chemical Shifts[b], ppm		DN	f(AN)
	exp.	cal.[a]		
Nitromethane	7.73	7.67	2.7	8.20
Dioxane	7.93	7.99	14.8	4.32
Diethyl ether	7.85	7.83	19.2	1.56
Tetrahidrofurane	8.23	8.28	20.0	3.20

[a]Calculated according to: $\delta(\text{N–H}) = a\,DN + bf(AN) + c$; a = 0.09; b = 0.20; c = 5.79. [b]Measured relative to tetramethylsilane.

comparable with the donor numbers; such an enthalpy scale can approximately be obtained by making use of the formula [31]:

$$\Delta H = \frac{AN \cdot DN_{(C_2H_5)_3PO}}{100}$$

where the donicity of triethylphosphine oxide has been estimated to be approximately 40. A similar method for describing the solvent effect on physicochemical properties of solutes has been proposed by Krygowski and Fawcett [32] using a relationship containing the Dimroth–Reichardt parameter E_T [33] and the Gutmann donor number DN [20]. Recently, while this paper was being prepared, an identical donicity–accepticity approach was applied to a number of thermodynamic and kinetic processes [34]. As is shown in Table II, there is a fair agreement between the calculated and experimental chemical shift values for NM, Dx, ether and THF by using this donicity–accepticity approach; the multiple correlation coefficient (r) and the mean square deviation (M.S.D.) are 0.9773 and 0.087, respectively. Among the solvents with low donicity ($DN \leq 20$) the point corresponding to PDC is anomalous (including PDC, r = 0.6870 and M.S.D. = 0.213). PDC is a large and bulky molecule [35], so that steric hindrance effects cannot be excluded in the interaction of the solvent with the thioacetamide molecule. A steric hindrance could prevent a simultaneous nucleophilic and electrophilic association with the PDC in a similar extent as that which occurs with the smaller molecule of other solvents. In the solvents with higher donor numbers (DMSO, DMA and HMPA) the chemical shifts appear to be mainly determined by the solvent donor strength. The downfield shifts observed in these solvents are relatively large with respect to those observed in solvents with lower donor numbers, in spite of the apparent small contribution of the electrophilic properties of the solvents. This behaviour could be explained assuming that a rota-

tion of the N–H_2 group out of the molecular plane S–C–N, with a change of the hybrid character at the nitrogen atom from sp^2 to sp^3, could occur. The stability loss produced by this rotation owing to the decreased electron delocalization could be compensated by a better hydrogen bonding interaction with the solvent. The influence of steric hindrances on the planar structure of thioamides has been recently discussed in a similar manner for the case of substituted aromatic thioamides [4] as well as for the behaviour of N-methylthiourea in solvent mixtures [36]. The same argument could also be valid for the behaviour of the thioacetamide complex solutions in DMA and HMPA observed in Fig. 2; here, apart from the induced steric hindrance, a higher solvent donicity would be necessary to produce the rotation due to the greater C–N bond strength induced by the formation of a coordinative bond at the sulfur atom.

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