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HYDROLYSIS OF ACETONITRILE IN THE PRESENCE OF $NbCl_5$

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Abstract—The mechanism of the hydrolysis of acetonitrile to ammonium ion in the presence of $NbCl_5$ has been investigated. Two possible mechanisms are discussed: metal-assisted (catalysed) hydrolysis and a mechanism based on the addition of alcohol and HCl to the CN triple bond to give initially an imidate hydrochloride salt, which may undergo further hydrolysis to the ester and ammonium ion (Pinner synthesis). Support for this route came from the spectroscopic identification of the alkoxyimminium ion intermediate, $CH_3C(OCH_3) = NH_2^+$. Although the reaction is not catalysed by Nb, the extent of reaction is strongly related to the amount of Nb present. It is concluded that the Pinner reaction is operating with the amount of HCl available for the reaction being controlled by the Nb concentration.

During work on the ^{93}Nb NMR on $NbCl_{5-x}(OR)_x$ ($x = 0$–5)[1] as sol-gel precursors,[2–5] we noticed that 2 days after adding MeOH to $(NbCl_5)_2$ in acetonitrile, crystals of ammonium chloride had formed in the NMR tube. Since the solvent is the only source of nitrogen present we concluded that the ammonium chloride was found as a hydrolysis product of the acetonitrile solvent, and further investigation showed that the solvent was not completely anhydrous. Acetonitrile hydrolysis is surprising since nitriles are generally resistant to hydrolysis,[6] e.g. the rate of hydrolysis is of the order of 10^{-6} M^{-1} s^{-1} for OH^- catalysed hydrolysis[7] or boiling with conc. H_2SO_4.[8] Here we present the results of our investigations into the mechanism of this hydrolysis reaction.

RESULTS

The weight of NH_4Cl crystals produced was initially used as a measure of the extent of hydrolysis since ammonium chloride is only sparingly soluble in acetonitrile. The number of moles of ammonium chloride produced would indicate whether the reaction was a catalytic one or not—if the value of the turnover (T) (T = number of moles of ammonium chloride/number of moles of Nb) exceeded 1, then the reaction would be catalytic. To measure the turnover, known quantities of water were added to 0.05 mol dm^{-3} solutions of $(NbCl_5)_2$ in acetonitrile with 3 equiv. of MeOH and left for 3 days. The ammonium chloride crystals formed were washed with cold acetonitrile, dried and weighed. It was found that the turnover reached a maximum at a value of 1, for two or more equivalents of water. Addition of further MeOH or water to solutions with a turnover of 1 did not cause further production of NH_4Cl. This means that the reaction is not catalytic.

The reaction was repeated with 1–4 equiv. of water, but this time no MeOH was added. None of the reactions produced ammonium chloride, however GCMS on the solutions did show trace quantities of acetamide were present. ^{93}Nb NMR of the solutions gave a single peak at -495 ppm, indicative of $Nb(OH)Cl_4 \cdot CH_3CN$ or $Nb(OH)Cl_3 \cdot (CH_3CN)_2$ species, and this was generally formed within minutes of addition to H_2O.

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NMR studies of reactants and products

In order to elucidate a mechanism for the hydrolysis, a series of NMR studies were undertaken. The studies had to be done in a coordinating solvent (deuterated acetonitrile) as the addition of water to solutions of $(NbCl_5)_2$ in non-coordinating solvents caused the immediate precipitation of Nb_2O_5. Thus 0.1 mol dm^{-3} solutions of $NbCl_5 \cdot (CH_3CN)$ and 0.05 mol dm^{-3} solutions of $NbCl_5 \cdot (PhCH_2CN)$ were prepared. To these solutions were then added either (i) 2 or 3 equiv. of H_2O; or (ii) 3 equiv. of MeOH and 2 equivalents of H_2O. Multinuclear NMR spectra were then run on these solutions to follow the reactions occurring.

In the $NbCl_5 \cdot (CH_3CN)$ cases it was observed that the CD_3CN exchanged with the bound CH_3CN to give a large free CH_3CN peak at 2.0 ppm in the ^1H NMR spectrum and presumably $NbCl_5$ (CD_3CN). No other species were observed, confirming that prior to addition of MeOH there is no nitrile hydrolysis, only the hydrolysis of $NbCl_5$ to the $Nb(OH)Cl_4$ species.

However, upon addition of MeOH and H_2O (3 and 2 equivalents, respectively) to solutions of $NbCl_5 \cdot (CD_3CN)$, many other species were observed. A summary of the NMR signals observed and their assignments is shown in Table 1. These NMR studies of the $NbCl_5 \cdot CH_3CN\text{–}H_2O\text{–}MeOH$ system confirmed a number of points:

(i) the reactions proceeded over about 3 days after this further reaction occurred only very slowly;

(ii) the free CH_3CN peak is unchanged, showing that only the bound acetonitrile, which is of course the deuterated form CD_3CN after exchange, has been hydrolysed;

(iii) that a turnover of 1 is observed for the 2 equivalents of H_2O and 3 equivalents of MeOH systems. This is deduced from the integrals of the ^1H signals in the product mixture for methyl ethanoate (CD_3COOCH_3) (2.9H), acetic acid CD_3COOH (0.1H) and the unreacted marker signal of free CH_3CN (3H). As this CH_3CN was present initially bound in a 1 : 1 ratio with $NbCl_5$ the ratio of hydrolysis products a Nb is 1 : 1 and thus confirms the turnover observed bythe gravimetric analysis of the ammonium chloride.

Similarly, the reaction of $NbCl_5 \cdot (PhCH_2CN)$ in CD_3CN with 3 equiv. of MeOH and 2 equiv. of H_2O produced CD_3COOCH_3 and CD_3COOH, the hydrolysis products of CD_3CN, with a turnover of ~0.8. This was unexpected as it was assumed the system would give the hydrolysis products of phenyl acetonitrile (*i.e.* methyl benzyloate, $MeOC(O)CH_2C_6H_5$), and phenyl acetic acid $PhCH_2COOH$). In fact the NMR spectra suggest that the $PhCH_2CN$ remains bound to Nb during the reaction.

In summary, the fact that the total number of moles of CD_3COOCH_3 and CD_3COOH produced was equal to the number of moles of ammonium chloride produced is consistent with two possible mechanisms: metal catalysed hydrolysis of bound nitriles; and the alcoholysis of the nitrile to the imidate hydrochloride (the Pinner synthesis). Of the two the Pinner synthesis is favoured for the reasons discussed below.

Table 1. NMR detection of products in the $NbCl_5CD_3CN$, MeOH, H_2O system (1 : 3 : 2)

			Species observed[a]		
NMR	$MeOC(O)CD_3$	NH_4Cl	$CD_3C(O)OH$	$NbCl_4OMe \cdot CH_3CN$	$NbCl_4OH \cdot CH_3CN$
^1H	3.675	6.20 (tr)[b]	9–10 (br)	4.20	
^2D	2.15			2.35	2.35
^{13}C[c]	18.4 (Sept), 51.0		19.1 (Sept)	59.9[d]	[d]
	171.3		178.6		
^{14}N		−356[e] (Sept)			
^{93}Nb				−560[f]	−495

[a] MeOH observed at 3.45 ppm in ^1H and 49.85 in ^{13}C NMR spectra.

[b] $J_{NH} = 53.5$ Hz, total peak area no more than 4% of CH_3CN peak area. Figures in parentheses are relative peak areas.

[c] Proton decoupled and DEPT spectra.

[d] Shoulder between 1 and 3 ppm due to CD_3.

[e] $J_{NH} = 54$ Hz.

[f] Decreases to ~70% of overall Nb species after 4 days.

Discussion of the possible mechanisms

(A) *Metal catalysed hydrolysis of bound nitriles.* Although nitriles are quite resistant to hydrolysis, a number of metal cations are known to catalyse hydrolysis. Thus the hydrolysis of nitriles is catalysed by Co^{III},[7] Rh^{III},[9] Ir^{III},[9] Ru^{III},[10,11] where the nitriles are coordinated to the metal, and by Cu^{2+}, Ni^{2+}, Zn^{2+}, where the nitrile function is covalently linked to the metal coordinating functionalities.[12,13] In all cases the nitrile is hydrated to the corresponding amide. Thus it is plausible that the bound acetonitrile was being hydrolysed to acetamide, and then further reacting to form ammonium chloride and methyl ethanoate, by the type of reaction shown in Fig. 1.

This mechanism would give an explanation as to why no hydrolysis was observed when water was added to the system, since catalytically inactive species such $NbOCl_3$ and $Nb(OH)Cl_4$ without coordinated acetonitrile are formed within minutes of addition of water. When methanol is present, however, ^{93}Nb NMR shows that a complex containing coordinated acetonitrile *i.e.* $NbCl_4(OMe) \cdot CH_3CN$ exists in equilibrium with $NbOCl_3$ in $MeOH$-H_2O systems and can thus by its presence catalyse the hydrolysis of bound acetonitrile.

However, a number of questions were left unanswered by this mechanism. First, the turnover measurements described above appeared to rule out a catalytic mechanism. Second, the formation of acetamide is never observed. Third, the addition of 3 equiv. of MeOH and 2 equiv. of H_2O to $NbCl_5 \cdot (PhCH_2CN)$ did not give the formation of methyl benzyloate, but rather the formation of methyl ethanoate. If the reaction was occurring by hydrolysis of bound nitriles, the production of benzylamide or methyl benzyloate would be expected, as Mukaiyama *et al.*[4] have shown that a mixture of $TiCl_4$/H_2O in a 1/2 ratio with hydrolyse benzonitrile to benzamide in a 90% yield. Because no free $PhCH_2CN$ was ever observed, the exchange of bound $PhCH_2CN$ with deuterated acetonitrile solvent can be ruled out, and direct metal involvement seems unlikely.

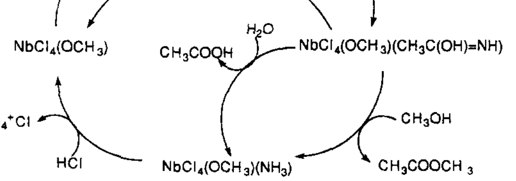
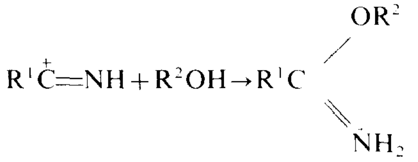


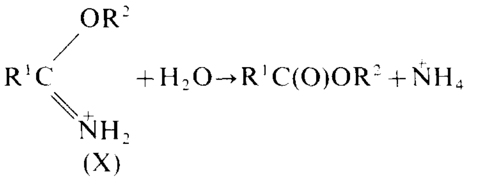
Fig. 1. Proposed mechanism for the metal-catalysed hydrolysis of acetonitrile.

(B) *The Pinner Synthesis.* The Pinner Synthesis is an important organic reaction for the production of imidates from nitriles and is also used as an alternative to the direct (base catalysed) hydrolysis of nitriles to give esters and carboxylic acids. The reaction proceeds by the route given in eqs (1)–(3):[8,15–17]

$$R^1C{\equiv}N \xrightarrow{H^+} R^1C^+{=}NH \qquad (1)$$



$$R^1\overset{+}{C}{=}NH + R^2OH \rightarrow R^1C(OR^2){=}\overset{+}{N}H_2 \qquad (2)$$



$$\underset{(X)}{R^1C(OR^2){=}\overset{+}{N}H_2} + H_2O \rightarrow R^1C(O)OR^2 + \overset{+}{N}H_4 \qquad (3)$$

Typically HCl is used as the catalyst and a primary or secondary alcohol as the alcoholating agent. The formation of the alkoxy iminium ion (X) usually takes between 12 and 72 h depending on R_1 and R_2. Hydration of the alkoxyiminium ion takes place instantaneously. Since attack by H_2O on the protonated nitrile is very slow and rarely observed, the water may be present throughout the reaction or added after the formation of X.[8] It is important to note that no metal ion is involved in this mechanism.

In support of the Pinner route to ammonium ion, we succeeded in identifying the intermediate X. Although X (methoxy methyl imidate hydrochloride, R_1 and R_2 = CH_3) is unstable in the presence of H_2O and decomposes to methyl ethanoate, we succeeded in isolating this intermediate from the reaction between $NbCl_5 \cdot CH_3CN$, CN_3CN and CH_3OH in a 1 : 1 : 3 ratio in toluene. After reaction at room temperature for 24 h the solvent was removed and the oil that remained gave ^{1}H NMR signals (in $CDCl_3$) at 2.60 and 4.35 ppm, in a 1 : 1 ratio, corresponded to literature values.[18] There was also a broad peak at −242 ppm in the ^{14}N NMR spectrum characteristic of imidates.[18]

The Pinner mechanism fits the experimental observations far better than the metal catalysed hydrolysis of bound nitriles. The reaction time is of the correct order. The fact that acetamide is not observed is to be expected. It also explains why no reaction with the bound phenyl acetonitrile was observed—MeOH and H_2O were reacting with the

$NbCl_5 \cdot PhCH_2CN$ to release HCl which then catalysed the alcolation of the solvent CD_3CN to give CD_3COOCH_3. Finally, the non-catalytic property of the reaction, with a turnover of unity, is now explicable: all the protons generated in this system come from the reaction of one Nb—Cl bond with ROH (where R = H or Me). This reaction yields only one proton and the species $NbCl_4(OMe) \cdot CH_3CN$ or $NbCl_4(OH) \cdot CH_3CN$. These latter species exist in equilibrium together and, under the reactions conditions observed, do not undergo further substitution and proton release. Therefore the single proton consumed by eqs (1)–(3) (the protonation of the nitrile) is formed by the single substitution of each Nb molecule and thus only a turnover of unity is observed. Normally the Pinner synthesis uses dry HCl gas as reagent. The control on the precise number of protons liberated by the use of metal chlorides such as $NbCl_5$ may be of interest in the Pinner reaction for the organic synthesis of compounds containing several sensitive groups.

Conclusions

The formation of ammonium chloride in acetonitrile solutions containing $NbCl_5$, MeOH and H_2O is due to the release of protons which catalyse the alcoholation of acetonitrile, by the Pinner Synthesis. This highlights the need for dry solvents in niobium(V) chemistry, and the unexpected reactions that can occur. Under the conditions described in this paper the formation of the protons occurs when the $NbCl_5$ is substituted by one ROH molecule and the number of protons is limited to one per $NbCl_5$.

EXPERIMENTAL

All preparative reactions were done under N_2 and in dry glassware (at 293 K except where noted), and *unless specifically noted all solvents, regardless of grade, were redistilled over* Na, 3 Å *molecular sieves or* CaH_2. ^{93}Nb NMR (coupled) were run on a Bruker MSL 500 spectrometer ($\tau_0 = \sim 500$ ms, $\tau_1 = 5$–20 ms), and ^{1}H NMR on AM300 or WP80 spectrometer. FTIR spectra were obtained on a Perkin–Elmer 1710 spectrometer, and Raman spectra on a Spex 1403 interfaced to a DM1B computer with Coherent Radiation Innova 90-6 Ar^+ laser excitation at 514.5 nm, power < 100 mW at the sample (spectroscopic data are within ± 1 cm^{-1}). Mass spectroscopy was obtained on an INCOS GCMS spectrometer. X-ray powder diffraction was run on a Stoe Stadi-P using Cu $k_{\alpha 1}$ radiation. SEM (Scanning electron microscopy) was performed on a Jeol JSM 35CF (15 keV) with scanning EDAX (energy dispersive analysis by X-rays) attachment at the Gatty Marine Laboratory.

UV–vis spectra were obtained on a Phillips PU8720 UV–vis spectrometer using a 0.5 mm path length cell. ESR spectra were obtained on a Bruker ER 200 D spectrometer with low temperature attachment. ^{93}Nb NMR were run on a Bruker MSL 500 spectrometer, ^{1}H on a WP80 and ^{2}D, ^{14}N on an AM300 spectrometer. FTIR (Perkin–Elmer 1720) and Raman (Spex 1403 interfaced to a DM1B computer with Coherent Radiation Innova 90-6 Ar^+ laser excitation at 514.5 nm, power < 100 mW at the sample) spectroscopic data are within ± 1 cm^{-1}.

Ammonium chloride

The ammonium chloride crystals produced by the hydrolysis of acetonitrile were washed with cold acetonitrile, dried at 80°C. FTIR matched identically that of commercial ammonium chloride (Aldrich, ACS reagent). Anal. Found: H, 7.5; N, 25.8; C, 0.9. Calc: H, 7.5: N, 26.2.

NMR studies of acetonitrile hydrolysis reactants and products

In order to elucidate a mechanism for the hydrolysis, a series of NMR studies were undertaken at 293 K. The studies had to be done in deuterated acetonitrile as the addition of water to solutions of $(NbCl_5)_2$ in non-coordinating solvents caused the immediate precipitation of $Nb_2O_5 \cdot 0.1$ mol dm^{-3} solutions of $NbCl_5 \cdot CH_3CN$ and 0.05 mol dm^{-3} solutions of $NbCl_5 \cdot PhCH_2CN$ were prepared. To these solutions were then added either: (i) 2 or 3 equivalents of H_2O; or (ii) 3 equivalents of MeOH and 2 equivalents of H_2O. Multinucle NMR spectra were then run on these solutions to follow the reactions occurring.

$NbCl_5 \cdot PhCH_2CN$. 1.35 g of $(NbCl_5)_2$ was dissolved in excess (20 cm^3) phenyl acetonitrile (Koch Light, puriss grade, redistilled over P_2O_5), and sonicated for 1 h at 60°C (under N_2). Removal of solvent gave a brown solid, $NbCl_5 \cdot PhCH_2CN$. ^{1}H spectra, 7.53 ppm, 5H (phenyl), 3.925 ppm, 2H (CH_2).

$Nb(OH)Cl_4 \cdot PhCH_2CN$. Addition of 2 or 3 equivalents of water to a 0.05 mol dm^{-3} solution of $NbCl_5 \cdot PhCH_2CN$ in CD_3CN gives $Nb(OH)Cl_4 \cdot PhCH_2CN$. ^{1}H spectra, 7.50 ppm (5H), 3.90 ppm (2H).

$NbCl_5 \cdot CH_3CN$. 1.35 g of $(NbCl_5)_2$ was dissolved in excess (20 cm^3) acetonitrile (Aldrich, anhydrous grade, redistilled over CaH_2), and sonicated for 1 h at 60°C (under N_2). Removal of solvent gave a yellow solid, $NbCl_5 \cdot CH_3CN$. ^1H spectra (in CD_3CN), 2.425 ppm (obtained by adding a further 10 equivalents of CH_3CN), ^{93}Nb spectra, −55 ppm.

$Nb(OH)Cl_4 \cdot CH_3CN$. Addition of 2 or 3 equivalents of water to a 0.1 mol dm^{-3} solution of $NbCl_5 \cdot CH_3CN$ in CD_3CN gave $Nb(OH)Cl_4 \cdot CH_3CN$. ^1H spectra, 2.325 ppm. ^{93}Nb spectra, −495 ppm.

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18. H. G. Viehe, H. Bohme, *Advances in Organic Chemistry* Vol. 9, Part 1, pp. 42–77. John Wiley, New York (1974), part (expected ^{14}N NMR in the range of −160 to −200 ppm, ^1H NMR R_1 ~2.6 ppm, R_2 ~4.35).