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Hydrogen bonding
Part 66. Further studies of the fluoride ion assisted dissolution of 1-methyl-4,5-dicarboxyimidazole: absence of cation participation and stoichiometric considerations

Kenneth M. Harmon*, Natalie J. LaFave

Department of Chemistry, Oakland University, Rochester, MI 48309 USA

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Abstract

Excess 1-methyl-4,5-dicarboxyimidazole (H_2MDCI) dissolves into saturated solution in the presence of sodium fluoride, and precisely four F^- are required for each H_2MDCI solubilized. To account for the apparent removal of two acidic hydrogens from H_2MDCI in the presence of undissociated diacid we postulated strong complexation of Na^+ by $MDCI^{2-}$. We now find that the dissolution behavior of H_2MDCI in the presence of either cesium or tetramethylammonium fluoride is identical to that with sodium fluoride. As cesium ion should bind weakly if at all to $MDCI^{2-}$, and tetramethylammonium ion should not be bound, we conclude that the cation present plays no role in the fluoride ion assisted dissolution of H_2MDCI. Analysis of dissolution stoichiometry and titration data suggests the possibility that two F^- react with H_2MDCI to form $HMDCI^-$ and HF_2^- and that two more F^- are required but do not act to abstract acid hydrogen. © 1997 Elsevier Science B.V.

Keywords: 1-Methyl-4,5-dicarboxyimidazole; Fluoride ion; Dissolution; Titrimetric analysis; Hydrogen bonding

1. Introduction

As part of a continuing study of the fluoride ion assisted dissolution of dicarboxylic acids into saturated aqueous solutions [1–3], we recently examined 1-methyl-4,5-dicarboxyimidazole [3], hereafter referred to as H_2MDCI. On the basis of IR and p*K*a evidence we proposed that H_2MDCI in the solid state was zwitterionic with one acid hydrogen in an unsymmetrical three-center covalent O–H–O hydrogen bond between carboxyl groups and the second acid hydrogen on N3, and with intermolecular hydrogen bonds between N3 hydrogens and carboxylate groups of adjacent molecules. This structure (Fig. 1) has recently been confirmed by diffraction studies (G. Hargrove and P.G. Rasmussen, personal communication, 1996). The IR spectrum of NaHMDCI and Na_2MDCI demonstrated that the more acid hydrogen (p*K*a = 3.60) is the O–H–O hydrogen, and the less acid hydrogen (p*K*a = 7.67) is the one on N3.

Dissolution studies showed that addition of sodium fluoride to a saturated solution of H_2MDCI in equilibrium with excess solid caused additional H_2MDCI to enter solution, and that precisely four F^- were required for each H_2MDCI so dissolved. This suggested that the dissolution process involved

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* Corresponding author.

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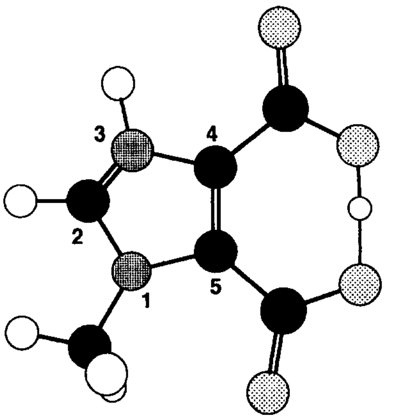

Fig. 1. Structure and numbering of H_2MDCI.

abstraction of both acid hydrogens from H_2MDCI to give $MDCI^{2-}$ and two HF_2^-. It did not seem reasonable, however, that F^- would remove the less acidic N3 hydrogen from $HMDCI^-$ in the presence of considerable undissociated diacid with more acidic O–H–O hydrogens, unless an additional driving force for this process was operative. As Rasmussen and Allan had shown [4] that a compound structurally similar to H_2MDCI formed an extremely tight complex with Na^+, we proposed that complex formation between $MDCI^{2-}$ and Na^+ provided the additional driving force for the removal of the second hydrogen from H_2MDCI [3].

To test this proposal we have now examined the dissolution behavior of H_2MDCI in the presence of cesium fluoride and tetramethylammonium fluoride (TMAF), to determine if changes in the complexing ability of the cation will affect the solution process.

2. Experimental

Anhydrous cesium fluoride (Aldrich, Milwaukee, WI) was used as supplied. Tetramethylammonium fluoride was prepared by neutralization of Aldrich 10% tetramethylammonium hydroxide solution with hydrofluoric acid and concentration in vacuo to a hard white solid; NMR analysis [5] showed 1.70 H_2O of hydration. Cesium fluoride and tetramethylammonium fluoride with 1.70 H_2O of hydration were handled in the glove box during preparation of solutions. H_2MDCI was kindly supplied by Professor Paul G. Rasmussen of the University of Michigan.

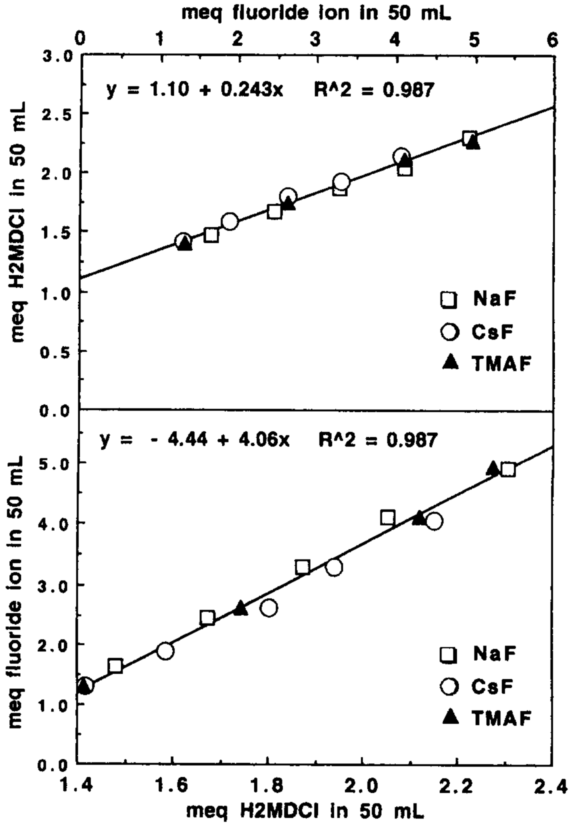

Fig. 2. Combined plots of titration data for dissolution of H_2MDCI with three fluoride salts. Curve fits are for all points.

Weighed portions of H_2MDCI were placed in 100 ml polyethylene bottles with a magnetic stirring bar and the appropriate amount of an aqueous fluoride salt solution of known concentration, and sufficient H_2O was added to bring the volume to precisely 50 ml. The samples were equilibrated with magnetic stirring for 24 h in a water bath at 25.0°C; then stirring was stopped and the solutions were filtered to remove undissolved acid while maintaining their temperature at 25°C. Aliquots of solution were withdrawn and titrated with standard NaOH solution using an Orion Research (Cambridge, MA) 200 pH meter. Endpoints were determined with Titration, a program developed at the University of Michigan Department of Chemistry. IR spectra were recorded on a Perkin-

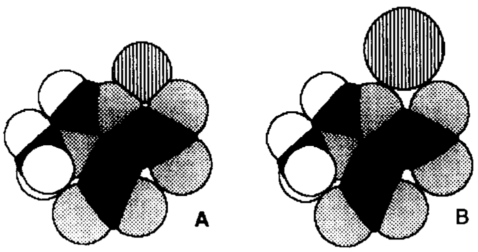

Fig. 3. Proposed interactions of $MDCI^{2-}$ with: (A) Na^+; (B) Cs^+ (see text).

Elmer (Norwalk, CT) Model 283 spectrophotometer as Nujol mulls on CsI plates. Molecular modeling and preparation of Fig. 1 and Fig. 3 (below) was done with Chem3D™ (Cambridge Computing, Cambridge, MA).

3. Results

There were no meaningful differences in the experimental results when either CsF or TMAF were substituted for NaF. The combined data for the solubility studies are shown in Fig. 2, and the values for slope and intercept for various plots of the data are listed in Table 1. In all cases, four F^- are required for each molecule of additional H_2MDCI taken into solution.

4. Discussion

4.1. Background

We have previously examined the dissolution of phthalic and succinic acid into saturated solution in the presence of added fluoride ion. Two F^- are required for each molecule of phthalic acid drawn into solution, and evaporation of a 2:1 NaF to phthalic acid solution yields sodium hydrogen difluoride and sodium hydrogen phthalate [1]. The solubilities of isophthalic and terephthalic acids are essentially unaffected by added fluoride. From these observations we concluded that the driving force for the dissolution of phthalic acid is the formation of two covalent three-center hydrogen bonds, F–H–F in hydrogen difluoride ion, and O–H–O in hydrogen phthalate ion. The process is thus

$$C_6H_4(CO_2H)_2 + 2F^- = \{C_6H_4(CO_2^-)_2H\}^- + HF_2^-$$

Succinic acid gave similar results; two F^- are required for each acid molecule taken into saturated solution, and the process is again driven by the formation of covalent hydrogen bonds in HF_2^- and the hydrogen succinate ion [2]. Alternative mechanisms for the dissolution process were eliminated by study of various model compounds [1,2].

H_2MDCI was the next dicarboxylic acid we chose to study, and a preliminary experiment showed that its solubility is increased in the presence of F^-. This seemed surprising when we later determined that H_2MDCI was a zwitterion with an O–H–O hydrogen bond between carboxylate groups already present, as we assumed that formation of such a bond was prerequisite for excess solubility in the presence of F^-. However, controlled studies confirmed this observation, and demonstrated that four F^- are required for each excess H_2MDCI taken into saturated solution [3].

Table 1
Numerical data for various plots of dissolution data

Salt	Plot[a]	Intercept	Slope	R^2
NaF[b]	A–F	1.06	0.249	0.997
CsF	A–F	1.08	0.263	0.997
TMAF	A–F	1.10	0.239	0.996
All points[c]	A–F	1.10	0.243	0.987
NaF[b]	F–A	− 4.23	4.00	0.997
CsF	F–A	− 4.10	3.78	0.997
TMAF	F–A	− 4.98	4.15	0.996
All points[c]	F–A	− 4.44	4.06	0.987

[a] F is milliequivalents of F^- salt in 50 ml; A is milliequivalents of diacid (H_2MDCI) in 50 ml.
[b] From [3].
[c] Combination plot of all points from the three fluoride salts.

4.2. The question of a cation effect

The fact that four F^- were required to draw one molecule of H_2MDCI into solution was unexpected, and raised immediate questions as to what the process could be. We had assumed that the role of F^- is to act as a base to remove acidic hydrogens; however, the fact that that the solubilities of isophthalic acid ($pKa_1 = 3.62$) or terephthalic acid ($pKa_1 = 3.54$) are not appreciably increased in the presence of F^- suggested that the simple process $HA + 2F^- = A^- + HF_2^-$ was not sufficient, and additional $-\Delta H$ of reaction was required. In the case of phthalic and succinic acid, this came from the formation of the strong intramolecular O–H–O bond.

In the case of H_2MDCI the most obvious stoichiometric explanation was that four F^- removed two acid hydrogens from one diacid molecule, thus drawing another into solution. This simple explanation is seriously flawed. It would require that the less acidic N3 hydrogens of $HDMCI^-$ react preferentially to form $MDCI^{2-}$ in the presence of a large excess of undissociated diacid with more acidic O–H–O hydrogens, and, for reasons discussed below, that H_2MDCI and $MDCI^{2-}$ coexist in solution. Both of these events seem extremely unlikely; if two hydrogens are removed from an H_2MDCI by four F^-, then some further factor must be involved to facilitate the removal of the N3 hydrogen and to stabilize $MDCI^{2-}$ in the presence of H_2MDCI.

A likely candidate for this additional factor was chelate type complexation of Na^+ (present from NaF) by $MDCI^{2-}$. Rasmussen and Allan [4] have reported that sodium 2-amino-4(5)-cyano-5(4)-imidazolecarboxylate cannot be protonated by strong mineral acid, and proposed that strong binding of Na^+ ion by this anion was responsible. As the N3 and one $-CO_2^-$ of $MDCI^{2-}$ provide an identical binding site to that of the 2-amino-4(5)-cyano-5(4)-imidazolecarboxylate ion, we proposed that a similar effect took place in the dissolution of H_2MDCI, and that complexation between $MDCI^{2-}$ and Na^+ was the additional factor which facilitated removal of N3 hydrogens.

We wished to test this hypothesis by repeating the dissolution experiments with H_2MDCI in the presence of other fluoride salts such as cesium and tetramethylammonium fluorides. The $O\cdots Na^+$ distances in crystals containing hydrated Na^+ ion are approximately 0.2 Å shorter than the sum of the Van der Waals radii [6,7]. If we allow a slight further shortening of this distance with the more basic sites in $NaMDCI^-$, molecular modeling shows that the Na^+ ion fits reasonably well for orbital interaction between $Na^+$and a $-CO_2^-$ group and the N3 (Fig. 3(A)). In crystals with hydrated Cs^+ ion the $O\cdots Cs^+$ distances are greater than the sum of the Van der Waals radii [7,8]. If the larger Cs^+ ion approaches $MDCI^{2-}$ at Van der Waals contact (Fig. 3(B)) the interaction angles are less favorable. This poor fit, coupled with the diminished propensity for the much softer Cs^+ ion to interact with bases relative to Na^+, suggested that cesium fluoride should not have any unusual effect on the dissolution of H_2MDCI, and that, if dissolution occurred at all, two F^- would be required and all O–H–O hydrogens would be removed before those on N3. This expectation was not realized; there is no significant difference between the effect of NaF or CsF on the dissolution of H_2MDCI.

Cesium ion, though much softer and less of a Lewis acid than sodium ion, is still an alkali metal ion, and complex formation cannot be completely ruled out. Therefore we have repeated the dissolution experiments with tetramethylammonium fluoride. TMA^+ ($r = 3.37$ Å) is much larger than Cs^+ ($r = 1.69$ Å) and has no empty orbitals to accept ligand electron pairs. Whereas TMA^+ can form $C\text{–}H\cdots X^-$ hydrogen bonds in crystals [9,10] it is unlikely to do so in solution. TMA^+ would not be expected to interact in any way with $MDCI^{2-}$ in aqueous solution. However, the effect of TMAF on the dissolution of H_2MDCI is indistinguishable from that of NaF. From the above, we conclude that the cation of the fluoride salt does not participate in any way in the dissolution process of H_2MDCI in the presence of F^-.

4.3. Ancillary observations

At this point, we can say that (1) four F^- are definitely required for each H_2MDCI taken into solution, and (2) the cation is not involved in the dissolution process. Several additional observations must be described, as they are essential for further discussion of possible mechanisms for the process.

The size of the samples of H_2MDCI weighed out was arbitrarily chosen so that approximately 50% of

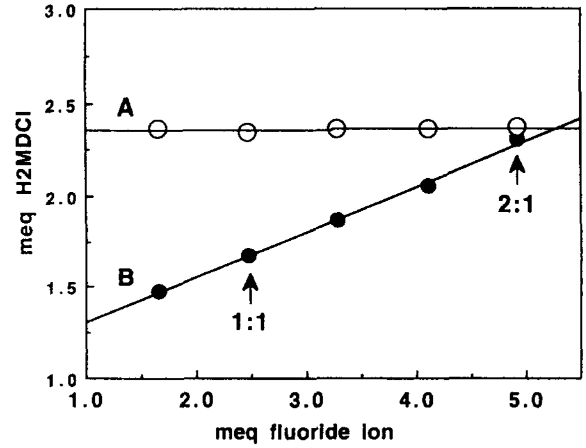

Fig. 4. Plots of: (A) total H_2MDCI (mequiv) in weighed sample; (B) H_2MDCI (mequiv) from sample in 50 ml H_2O vs. F^- in 50 ml H_2O.

the sample would dissolve in 50 ml H_2O before addition of fluoride salt. The actual value required to saturate the solution was found to be 47% of the total H_2MDCI. The quantity of H_2MDCI remaining after equilibration with fluoride salt diminishes with increasing amount of fluoride, and at a 2:1 F^- to H_2MDCI ratio the sample is almost completely dissolved (Fig. 4, Table 2).

All of the titrations of dissolution solutions show a two-step titration curve, and we now note that in every case the quantity of base required to neutralize the more acidic hydrogens is identical to that required to neutralize the less acid hydrogens (Fig. 5). The p*K*a of the first step gradually changes from 3.60 to 5.17 as the F^- to H_2MDCI ratio increases from zero to six, whereas the p*K*a of the second step remains essentially constant at 7.50 ± 0.16. From this, we conclude that the sum of $H_2MDCI + HF_2^-$ (first step) must at all times be equal to the amount of $HMDCI^-$ (second step).

Imidazole and its protonated form are easily distinguished. The NMR spectrum of the C–H protons of imidazole shows two singlets at 7.13 (2H) and 7.77 ppm (1H), whereas imidazole hydrochloride shows two similar singlets at 7.60 and 8.33 ppm. Equilibration of imidazole hydrochloride with two mole equivalents of CsF in concentrated aqueous solution for 4 days did not change the NMR spectrum at all. Excess fluoride ion does not remove the acid N–H hydrogen of imidazole (p*K*a = 6.95) and is thus unlikely to remove the N3 hydrogen of $HMDCI^-$ (p*K*a = 7.67). This, coupled with the titration data discussed in the preceding paragraph, strongly suggests that only O–H–O hydrogens are removed in the fluoride ion assisted dissolution of H_2MDCI.

4.4. Mechanistic discussion

The following discussion is based on the information and equations shown in Table 3. To avoid fractional coefficients the equations are written as though 50% of the H_2MDCI samples dissolved in 50 ml H_2O, rather than the actual value of 47%. We also assume for this discussion that the solubility of non-dissociated H_2MDCI in H_2O is not affected by the presence of fluoride salt.

If the only experiment run had been at a 2:1 initial ratio (eqn (1)) it would not be possible to determine if two or four F^- were consumed for each H_2MDCI. However, experiments at lower initial ratios confirm that the slope is four, and eqn (1) cannot describe the process. In addition, if only two F^- per H_2MDCI were required, then an initial ratio of 1:1 (and any ratio between 1:1 and 2:1) would result in total dissolution of the H_2MDCI sample (eqn (2)). This is clearly not the case (Fig. 4, Table 2).

Table 2
Per cent of total weighed sample of H_2MDCI in solution in 50 ml H_2O at various total H_2MDCI to NaF ratios

Run no.	Ratio H_2MDCI:NaF	H_2MDCI in total sample (mequiv)	H_2MDCI in solution (mequiv)	H_2MDCI in solution (%)
1	1:0.67	2.36	1.48	63
2	1:1.00	2.35	1.67	71
3	1:1.33	2.36	1.87	79
4	1:1.67	2.36	2.05	87
5	1:2.00	2.37	2.31	97

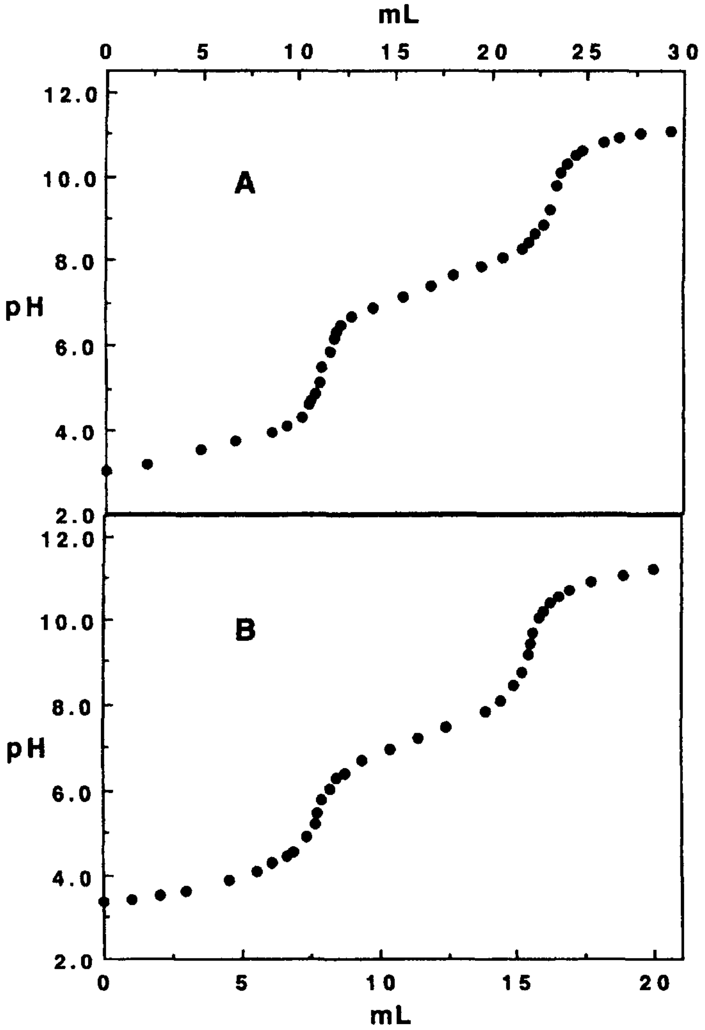

Fig. 5. Titration curve for: (A) H_2MDCI; (B) H_2MDCI treated with 2 mol equiv of CsI.

The simple assumption that four F^- remove both protons from an H_2MDCI to give $MDCI^{2-}$ (eqn (3)) gives the proper slope and solubility data, but would not yield the equivalent titration steps observed (Fig. 5). The coexistence of H_2MDCI and $MDCI^{2-}$ in solution appears impossible, and if they were to equilibrate to all $HMDCI^-$ the total sample would dissolve as in eqn (2). In addition, the failure of F^- to remove acid hydrogen from imidazole argues against removal of the N3 hydrogen of H_2MDCI in the absence of some additional effect. Stabilization of $MDCI^-$ by complexation with cation (eqn (4)) would obviate these problems and yield proper slope and solubility data, but cannot be reconciled with the equivalent steps in the titration curve or the identical action of NaF, CsF, and TMAF.

At present, we reach the somewhat unpalatable conclusion that the only process that seems to fit all of the experimental observations is one in which two F^- remove the O–H–O hydrogen from H_2MDCI, and two additional F^- are also required for dissolution of this molecule in some manner not associated with hydrogen removal from N3 (eqn (5) and eqn (6)). As tertiary amines have a propensity to form strong covalent three-center N–H–F hydrogen bonds to give molecular complexes [11–14] isolable from aqueous

Table 3
Comparison of predicted and observed results based on various dissolution mechanisms

Initial ratio F^-/H_2MDCI[a]	Fraction ratio F^-/H_2MDCI[b]	Predicted dissolution process[c]	Slope[d]	Predicted[e] % dissolution	Observed[f] % dissolution	Predicted[g] ratio H_1/H_2
2:1	2:1	$H_2MDCI(s) + H_2MDCI(aq) + 4F^-(aq) \rightarrow 2HMDCI^-(aq) + 2HF_2^-(aq)$ (1)	2	96	97	1:1
1:1	2:1	$H_2MDCI(s) + H_2MDCI(aq) + 2F^-(aq) \rightarrow H_2MDCI(aq) + HMDCI^-(aq) + HF_2^-(aq)$ (2)	2	96	71	1:1
1:1	4:1	$2H_2MDCI(s) + 2H_2MDCI(aq) + 4F^-(aq) \rightarrow H_2MDCI(s) + 2H_2MDCI(aq) + MDCI_2^-(aq) + 2HF^{2-}(aq)$ (3)	4	72	71	2:1
1:1	4:1	$2H_2MDCI(s) + 2H_2MDCI(aq) + 4F^-(aq) + 4Na^+ \rightarrow H_2MDCI(s) + 2H_2MDCI(aq) + NaMDCI^-(aq) + 2HF_2^-(aq) + 3Na^+$ (4)	4	72	71	2:1
1:1	4:1	$2H_2MDCI(s) + 2H_2MDCI(aq) + 4F^-(aq) \rightarrow H_2MDCI(s) + 2H_2MDCI(aq) + HMDCI^-(aq) + HF_2^-(aq) + 2F^-(?)$ (5)	4	72	71	1:1
2:1	4:1	$H_2MDCI(s) + H_2MDCI(aq) + 4F^-(aq) \rightarrow H_2MDCI{\cdot}F^-(aq) + HMDCI^-(aq) + HF_2^- + 2F^-(?)$ (6)	4	96	97	1:1

[a] Ratio of moles of F^- salt to total moles of H_2MDCI in sample (solid residue + solution).

[b] Number of F^- required for each H_2MDCI taken into solution.

[c] For simplicity, equations are written as though exactly 50% of H_2MDCI sample dissolves before reaction; the actual value is 47%.

[d] Slope of milliequivalents of F^- vs. milliequivalents of H_2MDCI expected for a given mechanism; the actual value is four in all cases.

[e] Based on actual solubility of H_2MDCI in 50 ml H_2O.

[f] From titration data.

[g] Predicted ratio of more acid hydrogen (H_1) to less acid hydrogen (H_2) in titrations; the observed ratio is 1:1 in all cases.

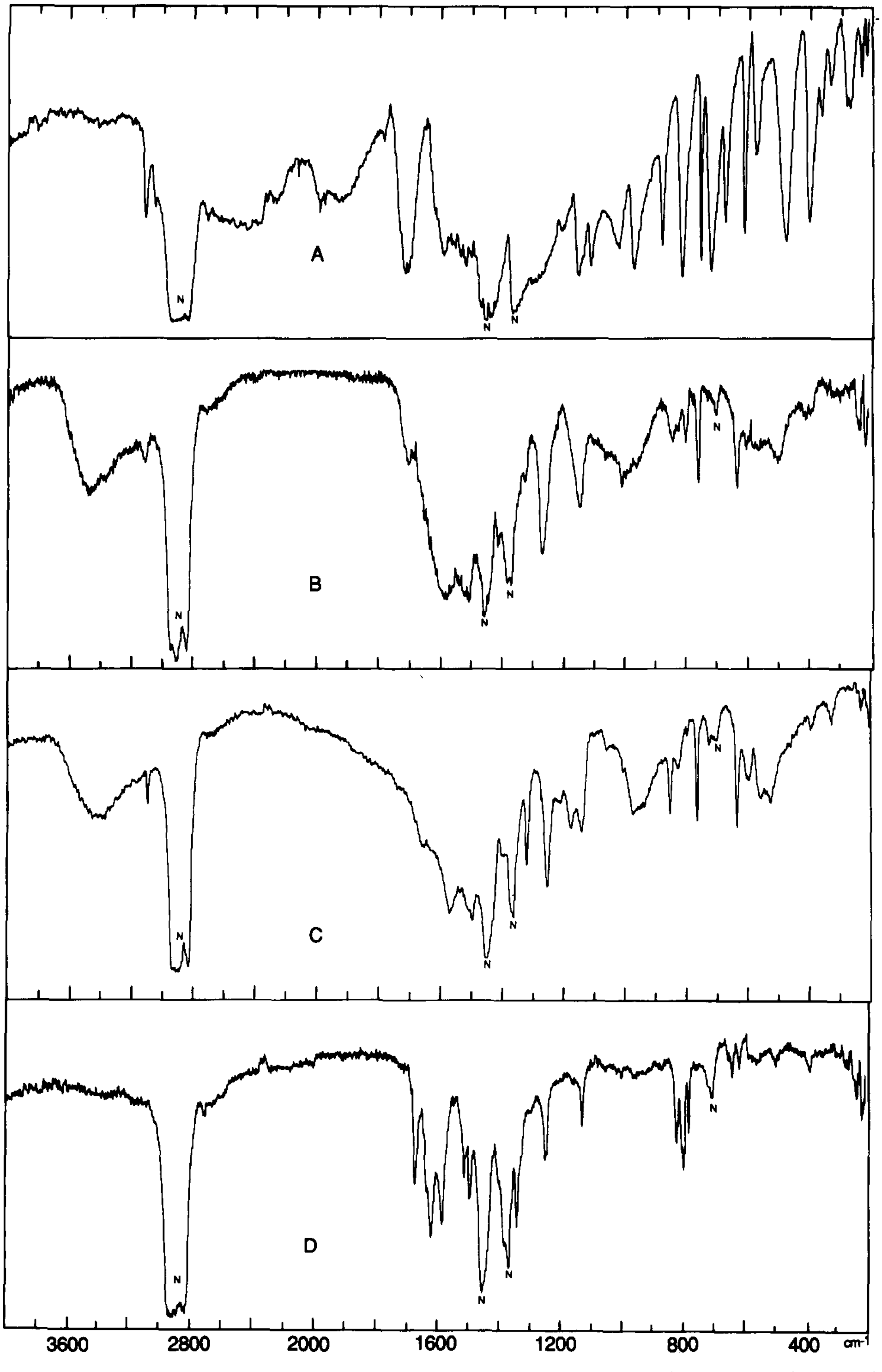

Fig. 6. IR spectra (Nujol mulls on CsI plates) of: (A) H_2MDCI; (B) NaHMDCI; (C) product isolated from concentration of 2:1 CsF to H_2MDCI solution; (D) Na_2MDCI. (Units are cm^{-1}; % *T*.) Peaks marked N are from Nujol.

Table 4
Stoichiometry of solids isolated from various mixtures of fluoride ion and H_2MDCI

Ratio F^-:H_2MDCI[a]	Reaction stoichiometry[b]	Solid species[c]
2:1	$H_2MDCI + 2A^+ + 2F^-$	$AHMDCI + AHF_2$
3:1	$H_2MDCI + 3A^+ + 3F^-$	$A_2MDCI + AH_2F_3$
4:1	$H_2MDCI + 4A^+ + 4F^-$	A_2MDCI + 2AHF2

[a] Sample sizes are such that the entire sample dissolves in 50 ml H_2O.
[b] A^+ is Na^+ or Cs^+.
[c] Solid mixture was obtained by evaporation of H_2O; compounds were identified by IR.

solution [14], a complex between F^- and $HMDCI^-$ could account for one additional F^-; however, the slope would then be three, not four. If similar complexing with non-dissociated H_2MDCI took place also, straight-line plots such as Fig. 2 should not be observed.

4.5. *The nature of solids isolated from fluoride ION–H_2MDCI solutions*

We have previously reported the nature of the solid material obtained by evaporation of 3:1 and 4:1 fluoride ion to H_2MDCI solutions [3], and now have examined the product from the 2:1 solution. The results of these studies are shown in Table 4. Regardless of what species may be in solution, the organic product of evaporation of a 2:1 solution is the monoanion $HMDCI^-$ with no H_2MDCI or $MDCI^{2-}$ present (Fig. 6). We assume that F^- is obtained as HF_2^-. However, as the sample was prepared with CsF, HF_2^- would constitute a very small proportion of the material (8.2% by weight), and only traces of the expected [15] IR bands can be observed. Evaporation of a 3:1 mixture yields $MDCI^{2-}$ and $H_2F_3^-$; thus with additional fluoride available both hydrogens are removed from H_2MDCI in the solid state, even though weaker F–H–F hydrogen bonds form. With sufficient fluoride present in a 4:1 ratio the products are $MDCI^{2-}$ and 2 HF_2^-.

There is no reason to assume that the stoichiometry of the solid state reflects what exists in solution at the concentrations used in the dissolution studies. However, the fact that it is possible under some conditions for F^- to remove the N3 hydrogen means that such abstraction cannot be unequivocally ruled out.

4.6. *Summation*

The precise mechanism for the fluoride ion assisted dissolution of H_2MDCI into saturated solution cannot be explained with the evidence now available. Detailed understanding of the molecular and ionic species present in the solutions is required, and we will shortly initiate FT-NMR studies in an attempt to elucidate this question.

5. Conclusion

1-Methyl-4,5-dicarboxyimidazole (H_2MDCI) is a zwitterionic compound with one acid hydrogen in an O–H–O hydrogen bond between carboxylate groups, and the other on a ammonium σ-orbital of N3. Excess H_2MDCI is taken into saturated solution in the presence of fluoride ion, and four F^- are required for each H_2MDCI so dissolved. Sodium, cesium, and tetramethylammonium fluorides give identical dissolution effects; therefore cation apparently plays no role in the dissolution process. Consideration of dissolution stoichiometry, titrimetric data, and the failure of F^- to ionize imidazole suggests that two F^- abstract O–H–O hydrogen from H_2MDCI to form $HMDCI^-$ and HF_2^-, and that two additional F^- are required for dissolution in some unknown manner that does not involve hydrogen extraction.

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