

THERMAL REACTION OF $\text{ClCH}_2\text{CONH}_2$ IN MOLTEN ACETAMIDE

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Abstract

Mixtures composed of amides and electrolytes exhibit interesting properties such as visco-elastic behaviour and a megavalence of the dielectric constant. In order to improve the dielectric properties, the authors are investigating a large number of molten mixtures of CF_3COONa with different types of amides, including the ternary system sodium trifluoroacetate-chloroacetamide-acetamide. The experimental measurements showed that the ternary mixtures are thermally unstable. A yellow oily product is formed; this was purified and tested by means of IR and NMR techniques. The formula and the kinetic mechanism are proposed.

Keywords: $\text{ClCH}_2\text{CONH}_2$, thermal reaction

Introduction

With a view to increasing the information available on molten electrolyte - amide systems, which exhibit interesting properties [1, 2], we have studied chloroacetamide to establish the influence of the chlorine atom on the structure of the mixture.

Experimental

The experimental cryoscopic technique employed has been described in previous publications [3, 4]. NMR and IR spectra were recorded on Varian 200 and Perkin-Elmer FTIR spectrometers, respectively.

Results

Figure 1 presents the liquid-solid equilibrium temperature vs. mole fraction for the binary system chloroacetamide + acetamide. This system is stable and

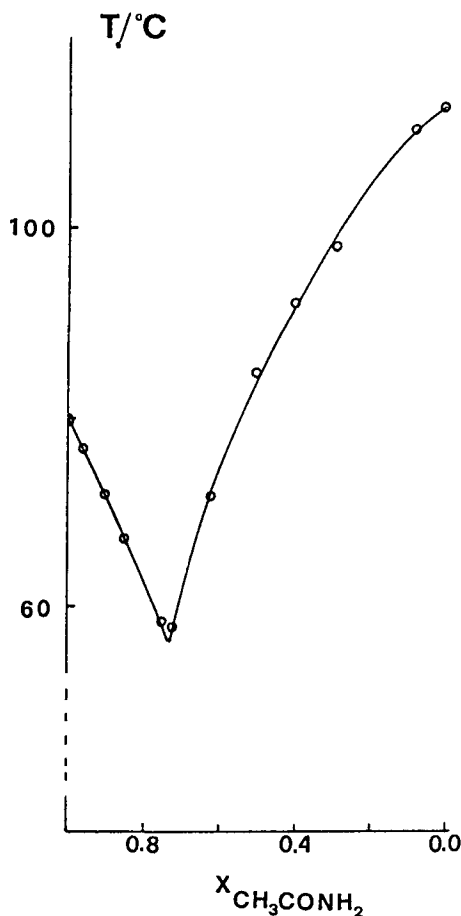
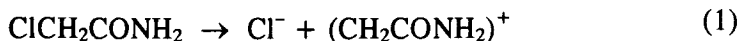


Fig. 1 Liquid-solid equilibrium temperatures vs. mole fraction of acetamide, for the binary system of acetamide and chloroacetamide

the melting temperatures measured at different times are reproducible. In contrast, when CF_3COONa is added to it, the mixture becomes unstable.

The ternary mixture ($\text{CH}_3\text{CONH}_2 : \text{CH}_2\text{ClCONH}_2 : \text{CF}_3\text{COONa}$ mole ratio = 7.318 : 1.963 : 1) darkens over 80°C , whereas the ternary mixture ($\text{CH}_3\text{CONH}_2 : \text{CH}_2\text{ClCONH}_2 : \text{CF}_3\text{COONa}$ = 3.118 : 0.836 : 1) decomposes rapidly, yielding a white precipitate and a yellow oily liquid. Filtration of the decomposed mixture led to a liquid (L) and a white powder composed to two types of crystals: lamellar (A) and microcrystalline (B). The A crystals were removed with forceps; both A and B crystals were purified by crystallization, from CHCl_3 (A) or from a $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ mixture (B). The purified A crystals melt at $119\text{--}120^\circ\text{C}$; the purified B crystals are cubic and very soluble in water.

Addition of a few drops of 0.1 M AgNO₃ to a solution of B yields a white precipitate of AgCl. Both the melting point and ¹H NMR spectrum of A indicate that A is ClCH₂CONH₂, whereas B is NaCl. The chemical nature of B shows that the chloride ion is produced by the thermal reaction in the chemical medium employed. That is, we suppose that in the studied mixture chloroacetamide decomposes in the first step according to the following equation:



Successively, *L* was diluted in ethanol, filtered and stored in the refrigerator overnight. Some translucent drops of a white oil (*C*) separated out in this period, and were removed and stored. The liquid (*L*₂) was concentrated by evaporation under dynamic vacuum to give a liquid *L*₃ and other drops of *C*, which were removed and added to the previously obtained drops. The liquid (*L*₃) was stored in a dry box for a long time in order to allow the complete precipitation of *C*, after which a chromatographic separation was carried out on silica gel, with a mixture of ethyl acetate (10 cm³) + cyclohexane (1 cm³) + 2 drops of 2 N ace-

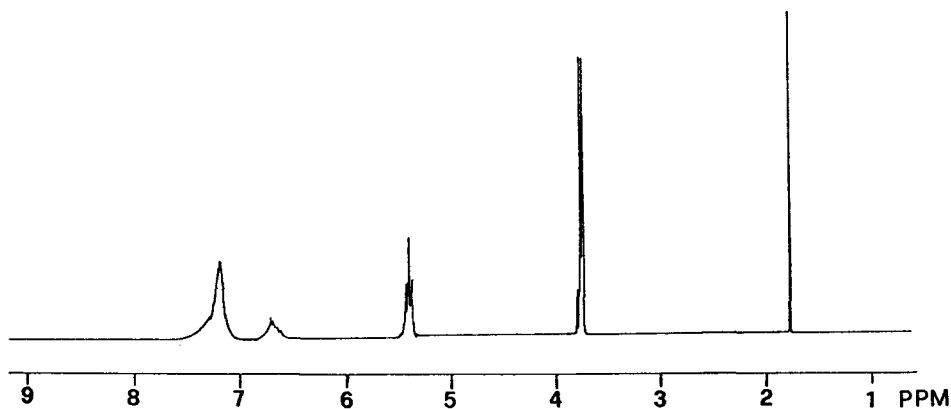


Fig. 2 ¹H NMR spectrum of the purified product obtained during the thermal reaction

Table 1

| δ/ppm | Hydrogen atom number ratio | D ₂ O exchange | Assignment |
|-------|-------------------------------|---------------------------|----------------------|
| 7.25 | 2 | no | <i>cis</i> -CH=N-O |
| 6.75 | (traces) | no | <i>trans</i> -CH=N-O |
| 5.4 | 1 | yes | OH |
| 3.8 | 2 | no | CH ₂ |

tic acid as eluent). These spots may be seen against the light: $L_{3,I}$ (rf = 0), $L_{3,II}$ (rf = 0.3) and $L_{3,III}$ (rf = 0.5). The product C was dissolved in ethanol: from this solution, white crystals with a melting point the same as that of A precipitated out after concentration. The spots $L_{3,I}$, $L_{3,II}$ and $L_{3,III}$ were separated and the corresponding products were extracted with methanol. The ^1H NMR spectrum of the total reaction mixture exhibited basically the absorption lines of acetamide, but in the δ region corresponding to the amidic group, besides the two absorption peaks of the amidic hydrogens (which disappeared when treated with D_2O), the two other low-intensity peaks were evident (which did not disappear when treated with D_2O). The ^{13}C NMR spectrum showed the presence

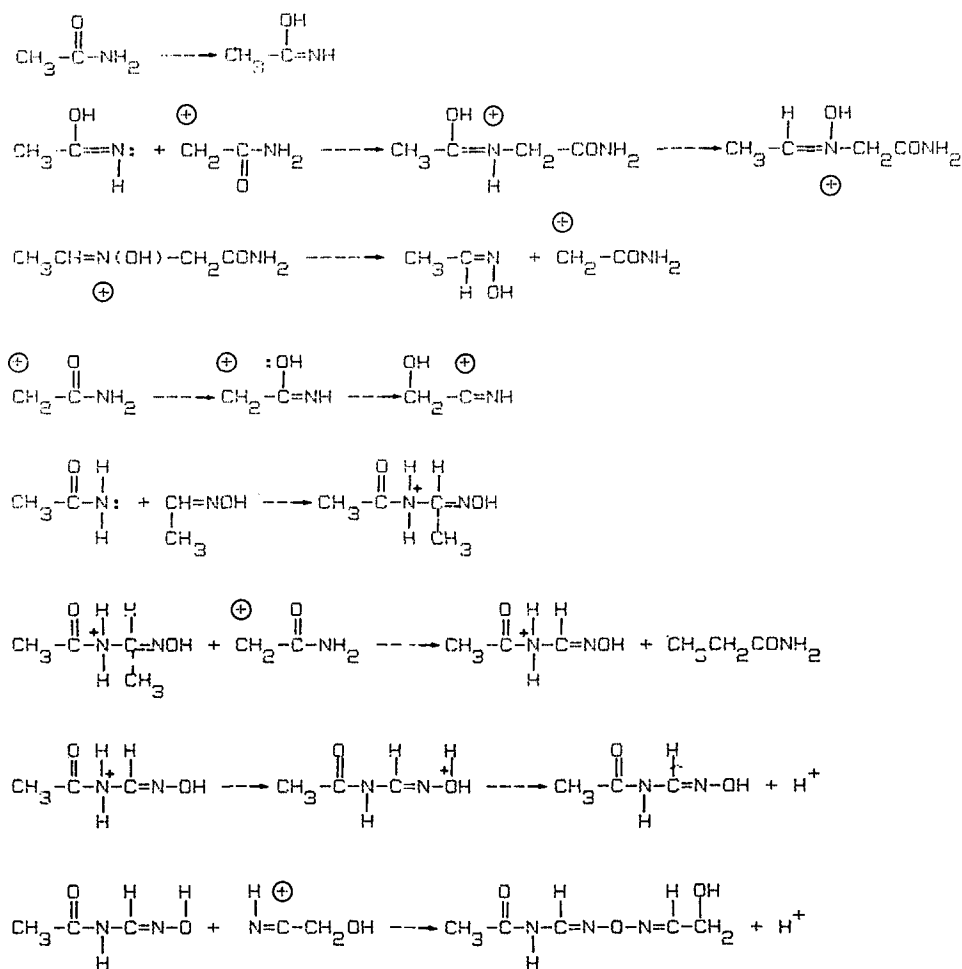


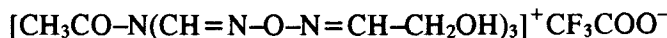
Fig. 3 Kinetic mechanism proposed to explain the formation of the new group $\text{CH}=\text{N}-\text{O}$

of acetamide, but also resonance at $\delta = 159.69, 159.06, 158.43$ and 157.82 ppm, characteristic of C=N-O, at $\delta = 126, 120.3, 114$ and 108.5 ppm, characteristic of CF₃, and at $\delta = 59.8$ ppm, characteristic of C-OH groups. The ¹⁹F NMR spectrum revealed a singlet resonance as regards the CF₃ group. The ¹H NMR spectrum of L_{3,II} is reported in Figure 2, and in Table 1 the explanation is given.

When the sample was treated with D₂O, the triplet signal at 5.4 ppm disappeared and the signal at 3.8 ppm changed from a doublet to a singlet, showing a coupling of the two types of protons. The spectra L_{3,I} and L_{3,III} had the same structure, but with some differences: L_{3,III} gave three signals in the range $\delta = 3-3.6$ ppm for protons which exchange with D, while L_{3,I} displayed two multiplets at $\delta = 0.8$ and 1.2 ppm; the absorption intensities of L_{3,I} and L_{3,III} were very low.

Conclusions

For the product mixture, the excess of acetamide covered the spectral lines of the principal product formed in the thermal reaction. After chromatographic purification, the principal product L_{3,II} demonstrated the presence of two new groups formed during the reaction: CH=N-O (*cis*) and CH₂OH. Since the product is conductive, we propose the formula



The probable mechanism of formation of group CH=N-O is proposed in Fig. 3.

References

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Zusammenfassung — Gemische aus Amidien und Elektrolyten weisen interessante Eigenschaften wie zum Beispiel viskoelastisches Verhalten und sehr hohe Werte für die Dielektrizitätskonstante auf. Zur Verbesserung der dielektrischen Eigenschaften wurde von den Autoren eine große Zahl geschmolzener Gemische von CF₃COONa mit verschiedenen Amidtypen untersucht, einschließlich des ternären Systemes Natriumtrifluoracetat-Chloracetamid-Acetamid. Experimentelle Messungen zeigen die thermische Instabilität dieses ternären Gemisches. Es wird ein gelbes ölarartiges Produkt gebildet, welches nach Reinigung mittels IR und NMR untersucht wurde. Formel und kinetischer Mechanismus werden vorgeschlagen.