

Note

**EFFECT OF ACOUSTIC RADIATION ON THE
THERMALLY UNSTABLE SYSTEM:
CF₃COONa + ClCH₂CONH₂**

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Introduction

An ultrasonic field may activate chemical reaction according to two principal theories: a thermal activation theory [1, 2] and an electric discharge theory [3]. An experiment to discriminate between these models does not yet exist [4].

We have recently shown that molten binary mixtures of CH₃CONH₂ and ClCH₂CONH₂, which are thermally stable, become unstable when CF₃COONa is added as third component [5]. The rapid reaction produces a viscous oily liquid, which from a spectroscopic point of view shows the presence of new groups: CH=N-O and CH₂OH. To explain the final product, we hypothesized the thermal breaking of the C-Cl bond of ClCH₂CONH₂ and attack by the carbonation on CH₃CONH₂.

The cavitation phenomenon, in an acoustically intense field, gives rise to a locally high value of temperature [1, 2], which can increase to several thousand degrees. With the aim of extending the possibility of study and application of this reaction to different media at room temperature, we have now studied a mixture of CF₃COONa and ClCH₂CONH₂ in aqueous solution in the presence of organic substances capable of reacting with a strong acid such as (CH₂CONH₂)⁺ under intense acoustic radiation. The organic substances present in the reaction mixture were adenine and ribose.

Experimental

An aqueous solution with the composition adenine : ribose : $\text{ClCH}_2\text{CONH}_2$: $\text{CF}_3\text{COONa}:\text{H}_2\text{O}=0.0020:0.0020:0.0032:0.0022:1$ (in mole) was sonicated with a Horn sonicator at 20 kHz and 90 W/cm^2 for 20 h. The solution was stored for 40 h at 80°C , after which it was filtered and the powder and liquid phases were separated by chromatography. Two products were obtained, denoted by A and B.

Results and discussion

a) Spectral identification of A was carried out by means of NMR (both ^{13}C and ^1H) and IR spectroscopy (^1H NMR data are to be seen in Fig. 1). Molecular mass and elemental analyses too were performed.

The product was identified as

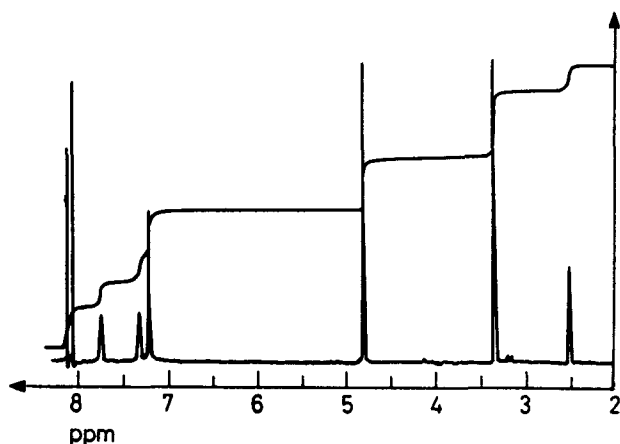
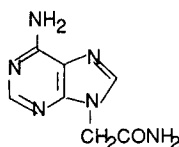


Fig. 1 ^1H NMR spectrum of product A

b) B is a more complex compound, obtained by conjugation of adenine and ribose. Its NMR, shown in Fig. 2, agrees completely with the published spectrum of adenosine [6]. When the experimental conditions were changed, and CF_3COONa was not present in the reaction medium, products A was again evident; in contrast, traces of adenosine were present.

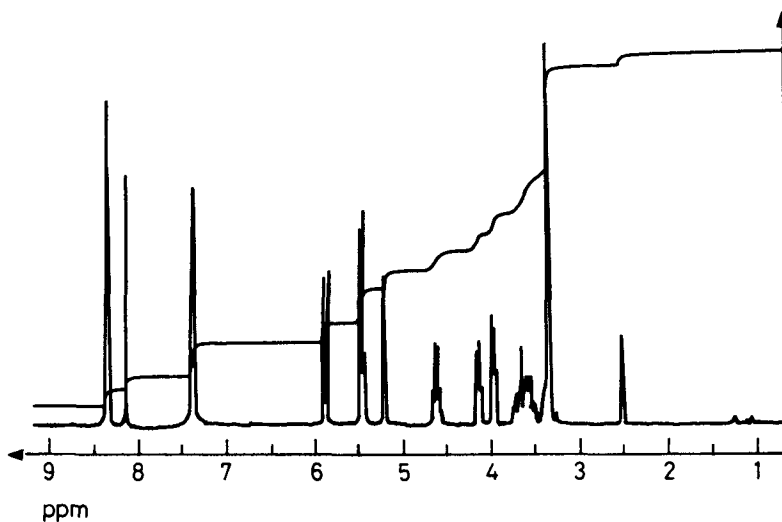
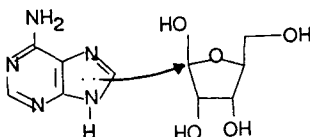


Fig. 2 ^1H NMR spectrum of product B

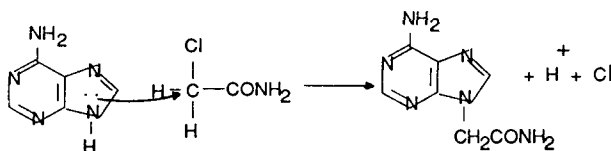
If neither CF_3COONa nor $\text{ClCH}_2\text{CONH}_2$ was present, adenosine was not produced. With regard to the micellar nature of CF_3COONa mixtures [7, 8], these findings suggest the following considerations:

- 1) adenine+ribose, regarded as a base-acid reaction,



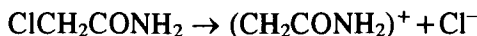
does not occur in the chemical medium employed, even if thermal energy is supplied to the system via ultrasonic cavitation.

- 2) In the presence of $\text{ClCH}_2\text{CONH}_2$, the acid-base reaction



occurs, but the analogous reaction 1 with sugar does not occur.

3) In the presence of both $\text{ClCH}_2\text{CONH}_2$ and CF_3COONa (and consequently in the presence of a micellar system [7, 8], the formation of a stronger acid (stabilized on the micelle) must be hypothesized, as previously done [5]:



which successively activates ribose. A kinetic study is needed to confirm this hypothesis. Moreover, the fact that the mixture $\text{CF}_3\text{COONa} + \text{ClCH}_2\text{CONH}_2$ is thermally unstable [5] supports a thermal mechanism rather than an electric one for the reactivity in the collapsing bubbles of the present system.

References

- 1 K. S. Suslick, 'Ultrasound, its Chemical, Physical and Biological Effects', VCH Publishers, N.Y., 1988.
- 2 T. J. Mason and J. P. Lorimer, 'Sonochemistry, Theory, Applications and uses of Ultrasounds in chemistry', Ellis Horwood Lim., Chichester (UK), 1988.
- 3 M. A. Margulis, *Advances in Sonochemistry*, 1 (1990) 39.
- 4 R. A. Roy, *Physical Aspects of Sonoluminescence from Stable Cavitation*. Third meeting of the sonochemistry, Figueira da Foz, Portugal, 28 March 1993.
- 5 G. Berchiesi, G. Vitali and F. Farhat, *J. Thermal Anal.*, in press (1994).
- 6 C. J. Pouchert, *The Aldrich Library of NMR Spectra*, Ed.II, 2^o, 597-c, Aldrich Chemical Company, Inc., 1983.
- 7 G. Berchiesi and F. Farhat, *Materials Science Forum*, 126-128 (1993) 367.
- 8 G. Berchiesi, F. Farhat, *J. Mol. Liquids* 51 (1992) 39.