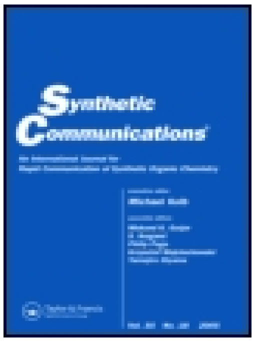

Synthetic Communications

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: F. FarhatG. Berchiesi (1992) Sonochemically Induced Reaction Between Water and 3-Chloropropionitrile, Synthetic Communications, 22:21, 3137-3140, DOI: 10.1080/00397919209409264

To link to this article: http://dx.doi.org/10.1080/00397919209409264

SYNTHETIC COMMUNICATIONS, 22(21), 3137-3140 (1992)

SONOCHEMICALLY INDUCED REACTION BETWEEN WATER AND 3-CHLOROPROPIONITRILE

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Abstract : The water-3-Chloropropionitrile biphasic system reacts in an ultrasonic bath, producing the corresponding amide, at room temperature. The C-Cl bond does not react; in this sense the attack is selective.

The use of ultrasounds to enhance chemical reactions by the cavitation phenomenon is of increasing interest[1-7] In spite of the simple mechanism of the cavitation, the sonochemistry is affected by a variety of parameters. We would like to begin a wide study on the influence of the chemical structure of the compound or its physical state on the sonochemical reaction.

EXPERIMENTAL

An ultrasonic cleaner manufactured by Heat Systems (Model 7E) is employed. It operates at 20 kHz and dis-

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sipates 0.775 W cm^{-2}. The sample contained in a 50 mL flask is tightly fixed just above the bottom of the sonicator bath. Circulation of water in a copper coil placed in the bath allows the temperature to be kept at nearly 20°C ± 1°C. The chemicals are 3-Chloropropionitrile from Aldrich Chemie (98%) and distilled water, previously aerated by insufflation.

The sonolysis of CCl_4/H_2O biphasic system in presence of KI[8] is carried out to check if the ultrasonic energy reaches the cavitation treshold.

^1H NMR and IR spectra are obtained using a 300 MHz Varian and a Perkin Elmer 1600 Series FTIR spectrometers respectively.

The chloropropionitrile and water biphasic system (1 mL, C_3H_4NCl + 10 mL, H_2O) is sonicated approximately 1 hour, then the sonication is stopped and the aqueous phase is separated and evaporated. This procedure is repeated 30 times and a brown solid product is obtained. A thin layer chromatography (silica gel) on the product shows the presence of a principal product and some impurities. The product was purified by recrystallization from $C_2H_2Cl_2 + C_6H_{12}$, 1:1 in volume, added with 3 drops of methanol and 0.070 g of a white crystalline powder (A) were obtained. After filtration the liquid is added of few mL of C_6H_{12} and some drops of a red oil precipitate from the liquid (B).

<u>A</u> : the NMR spectrum of the purified sample dissolved in dimethylsulfoxide shows two triplets at 2.5 and 3.7 ppm, which may be ascribed to two CH_2 groups, and a double si-

gnal at 7.0-7.2 ppm which is an evidence of the amidic group presence. IR spectrum shows two peaks at 3158.6 and 3333.6 cm^{-1}, characteristic of amidic NH_2, two peaks at 1633.7 and 1681.9 cm^{-1} of amidic CO. Also the chlorine peaks at 699.7 and 808.3 cm^{-1} are evident.

The melting point is 104.8°C at the second fusion. The analysis on C, H and N (33.59; 5.76; 12.61 %) gives the following ratio: C:H:N = 3:6:1, the same ratio as in chloropropionamide. The mass spectrum shows evidence of the presence of chlorine in the molecule. It may be concluded that in the described system the following reaction takes place:

$$ClCH_2CH_2CN + H_2O \longrightarrow ClCH_2CH_2CONH_2$$

whereas the chlorine atom does not react.

This is a different behaviour in comparison to the CCl_4/H_2O system. In order to ascertain if CCl bond may be attacked in the described conditions, we put 1 mL of Chloropropionitrile in 100 mL of water and this system was sonicated till the organic phase disappears and after this, the sonication continued for 36 hours. The chlorine tests did not show the formation of chlorine.

B : the NMR spectrum performed on the oil drops dissolved in dimethyl sulphoxide, shows the presence of all the lines exhibited by the amide and a very low intensity broaden double line in the 9 ppm region.

ACKNOWLEDGMENTS

Thanks are due to Prof.P.Franchetti for having put at our disposal the chromatographic devices and for having encouraged this research.

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(Received in The Netherlands 29 June, 1992)