

PROTON-TRANSFER IN 1,1,3,3 TETRAMETHYL GUANIDINE BY MEANS OF ULTRASONIC RELAXATION SPECTROSCOPY AND MOLECULAR ORBITAL CALCULATIONS

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ABSTRACT

Guanidines are a group of organic compounds sharing a common functional group with the general structure $(R_1R_2N)(R_3R_4N)C=N-R_5$. The central bond within this group is that of an imine, and the group is related structurally to amidines and ureas. An example of guanidines is the 1,1,3,3, tetramethyl guanidine which is studied in detail using vibrational and ultrasonic techniques in the present work. Most guanidine derivatives are in fact salts containing the conjugate acid with a variety of applications in industry and biochemistry^[1-2].

Liquid 1,1,3,3 tetramethyl guanidine (TMG) corresponding to molecular formula $(CH_3)_2NC(=NH)N(CH_3)_2$ of high purity (99.9%) was obtained from Aldrich. TMG is an organic colorless liquid. This amine is a strong base with a higher pKa than typical amines. No further purification was attempted. Solutions of TMG dissolved in triple distilled water were prepared gravimetrically by using standard procedures. Caution must be taken in the handling of TMG because eye damage and/or blindness may occur in case of contact with the eyes. It is interesting experimental observation was that when TMG was cooled then the supercooled liquid became increasingly viscous, while fast quenching resulted in a glassy material.

Ultrasonic techniques belong to the stationary relaxation techniques and their use depends on the frequency range of interest. These techniques cover the 10^4 to 10^{10} Hz frequency region, which means that one may perform relaxation times measurements in wide time scale, namely between 10^{-5} to 10^{-11} seconds. These very short times are difficult to be measured by other transient techniques and thus acoustic techniques have been proved a powerful and less expensive tool in describing the dynamic picture of a molecular system. Furthermore, an additional advantage of ultrasonic techniques is that there are no restrictions on the type of processes that can be studied.

Despite the large amount of studies concerning the structure and dynamics of aqueous solutions of non-electrolytes by ultrasonic methods, much less attention has been paid to the aqueous solutions of guanidine derivatives and to the interpretation of the underlying absorption mechanism. The purpose of our study is to provide comprehensive understanding on the structure and dynamics of the aqueous solutions on non-electrolytes by combining vibrational and ultrasonic spectroscopies. We report on the proton transfer reaction occurring in aqueous TMG solutions by measuring ultrasonic absorption and velocity as a function of concentration and temperature. The results are discussed and compared with analogous aqueous solutions of alcohols. The possibility of formation of other product during hydrolysis of TMG has been elucidated using Raman spectroscopic data.

Θεματικές ενότητες:

Φυσικοχημεία – Θερμοδυναμική

Βασική και Εφαρμοσμένη Χημεία

Προτεινόμενος τρόπος παρουσίασης: poster

LITERATURE

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