

Experimental and Theoretical Studies on Thermal Isomerization Reaction of Methyl 4-(Dimethylamino)-benzenesulfonate in the Crystalline State

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Solid-state thermal isomerization reaction from methyl 4-(dimethylamino)benzenesulfonate to *N,N,N*-trimethylbenzeneaminium-4-sulfonate has been studied by X-ray diffraction and spectroscopic experiments and *ab initio* MO calculations. The examination of the experimental results in comparison with the calculated results such as molecular total energies, intramolecular charge distributions, a transition-state structure, intrinsic reaction coordinates and lattice energies has provided us with much essential information to elucidate the process, mechanism and energetics of the reaction.

Keywords: Organic solid-state reaction/ Thermal isomerization/ Methyl cation transfer/ *Ab initio* MO calculation

In searching for an organic solid-state reaction which could be employed as a phenomenon deriving novel electronic properties with dynamical natures, the thermal isomerization reaction from methyl 4-(dimethylamino)-benzenesulfonate (MDBS) to a zwitterion of *N,N,N*-trimethylbenzeneaminium-4-sulfonate (TBS) in the crystalline state has been studied by both experiments of X-ray diffraction, infrared absorption, electronic absorption and emission and *ab initio* MO calculations using the RHF/MP2/6-31G* method to elucidate its mechanism [1,2], since this reaction is characterized by intermolecular methyl cation transfer.

This reaction can admit two kinds of ionic intermediates, that is, 4-(dimethylamino)benzenesulfonate (A, anion intermediate) and methyl *N,N,N*-trimethylbenzeneaminium-4-sulfonate (C, cation one), and they should exist at high concentrations during the reaction according to the two-step mechanism which was hitherto accepted. However, by comparing changes in

infrared absorption spectra through the reaction with the results from normal vibration analyses of the four chemical species involved by the RHF/6-31G* method, it is shown that concentrations of both intermediates have been less than the observation limits by the infrared absorption spectroscopy applied. This indicates that the thermal isomerization above proceeds not as a two-step reaction but as a chain one.

Concerning the heat of this reaction, *i.e.* $\Delta_f H^\circ \approx -63 \text{ kJ mol}^{-1}$, an interpretation that it is derived directly from the energy difference in total energies of MDBS and TBS in the isolated states seems to be contradictory to the results of lattice energy calculations of the two materials by other workers. To solve this problem total energies of both species in the isolated states were calculated with taking account of the electron correlation, and it has been clarified that MDBS is more stable than TBS by about 90 kJ mol^{-1} when their geometrical structures are kept to be the same as those in the respective single crystals. Further,

INTERFACE SCIENCE — Molecular Aggregates —

Scope of research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric properties. The electronic structure of organic thin films is studied using photoemission and inverse photoemission spectroscopies in connection with the former, and its results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with heterogeneous structures in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.



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lattice energies of both crystals have been re-evaluated using the intramolecular charge distributions obtained from those calculations to show that the heat of reaction is realized by the large difference of lattice energy overturning the difference of molecular total energy as a result [1].

The initiation reaction of the thermal isomerization reaction in the crystalline state can be expected to be a methyl cation transfer between two neighboring MDBS molecules. Such a structure that the methylsulfo group of a MDBS molecule looking on the nitrogen atom of the adjacent molecule is characteristic of the molecular structure of MDBS in the crystal, which is different from that resulted from the geometrical optimization calculation of an isolated molecule, and is suitable for the isomerization reaction. This notable conformation of the methylsulfo group is explained by the molecular structure stabilized by the molecular packing in the crystal [2].

Further, the geometrical optimization calculations of the reaction transition state derived from a pair of two MDBS molecules placed in the free space have been carried out using the RHF/6-31G* method to consider the initiation stage of the reaction, since any *ab initio* MO methods to calculate the transition-state structure with taking account of crystal field effects and the arrangement of a pair of molecules in the crystal as the initial structure that are expected from the sound scientific point of view

have not yet been established so far. A concerted form of the transition state with a coordination number of five for the carbon atom of the transferring methyl cation was obtained as the optimized structure from those calculations. Normal vibration analysis for this structure shows only one vibrational mode with an imaginary wavenumber at $562.90i\text{ cm}^{-1}$ that corresponds to intermolecular transfer of the methyl cation being detached from an O atom of the methylsulfo group in one MDBS molecule and connected with the N atom of the dimethylamino group in the other molecule. By examining the results of intrinsic reaction coordinate calculations around the transition-state structure in comparison with the geometrical arrangements of the atoms in the MDBS crystal to be involved in the reaction, it is implied that the cooperative rotation of molecules around their long axes coupled with the molecular structural deformation can bring about a notable structure characteristic for the transition state of the initiation reaction [2].

References

1. Oda M and Sato N, *Chem. Phys. Lett.*, **275**, 40-45 (1997).
2. Oda M and Sato N, *J. Phys. Chem. B*, **102**, 3283-3286 (1998).

Structure-Function Relationships in Alamethicin Ion-Channels: Effects of a Gln7 to Glu7 Mutation

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Effects of a Gln7 to Glu7 mutation in alamethicin on its ion-channel properties have been studied by the single-channel recording with planar bilayer lipid membranes. The mutation affected the channel conductance, current-voltage relationship, and ion-selectivity.

Keywords : Ion-channel/ Alamethicin/ Ion transport/ Bilayer lipid membrane

Alamethicin, a 20-residue peptide isolated from *Trichoderma viride*, forms ion-channels in artificial bilayer lipid membranes. The ion-channels, in which alamethicin helices are packed together in a parallel fashion around a central ion permeable pore, are basically similar to the pore region of biological ion-channels and therefore provide a useful model system for analyzing the ion transport mechanism of ion-channels. In the alamethicin ion-channels, the hydrophilic residue Gln7 faces the pore space and locates in the middle of the channels, being expected to play a key role in channel stability and ion transport. In this study, we have examined effects of a mutation of Gln7 to Glu7 with a negative charge on ion-channel formation and ion transport properties.

Native alamethicin (Gln7) showed ion-channels with six conductance levels, which may correspond to helix-

bundles of 4-9 peptides. The replacement of Gln7 with Glu7 had little effect on the channel stability but considerable effects on the ion transport properties as follows: (1) The frequency of occurrence of the levels 1 and 2 was extremely reduced. (2) The ion-channel conductance increased for all the levels. (3) The current-voltage relationships changed from a supralinear form to a linear one at low levels and from a linear form to a sublinear one at high levels. (4) The ion selectivity between K^+ and Cl^- changed from a non-selective type to a K^+ -selective one for all the levels. These findings suggest that the introduction of Glu7 with a negative charge induces (1) an increase in pore size by electrostatic repulsion between adjacent helices, (2) some reduction in the height of energy barrier for ion transport in the channels, and (3) high cation-selectivity.