

Thermal Solid-State Reaction of Methyl *p*-Dimethylaminobenzenesulfonate to *p*-Trimethylammoniumbenzenesulfonate Zwitterion: Optical Crystallographic Studies

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Received: July 23, 1999

The thermal isomerization reaction from methyl *p*-dimethylaminobenzenesulfonate (MSE) to *p*-trimethylammoniumbenzenesulfonate zwitterion (ZWT) in the crystalline state has been studied by optical crystallographic methods. Clear evidence of the lattice transformation occurring at ~60% conversion is provided by direct polarized light observations and by measurements of the birefringence Δn_{bc} and the optic axial angle $2V$. Until the transformation the monoclinic MSE lattice remains optically homogeneous and highly crystalline. During the whole reaction course the orientation of the optical indicatrix is constant, within one degree, but the parameters of the indicatrix progressively and markedly change. The direction of the highest refractive index corresponds, both for the starting MSE lattice and finally formed ZWT lattice, to the long molecular axis. Crossed axial plane evolution to a substantial $\sim 48^\circ$ was found. A wider use of the birefringence methods in investigations of solid-state chemical reactions is suggested.

Introduction

Organic solid state reactions occur usually under strict crystal lattice (topochemical) control.¹ Many thoroughly studied examples of crystal-directed product formation (concerning isomerization, dimerization, and polymerization reactions, activated both thermally and photochemically) are described in numerous recent reviews, for example.^{2–4} New and diverse reactions which modify the states of the molecules in the crystalline media are being developed and studied in many laboratories; one can even say that solid-state reactions have now entered into the mainstream of organic chemistry.⁵

One of the interesting topochemical, thermally-induced solid-state reactions is the methyl transfer isomerization reaction taking place in crystals of methyl *p*-dimethylaminobenzenesulfonate (MSE). An intermolecular migration of the methyl group yields the zwitterionic product *p*-trimethylammoniumbenzenesulfonate (ZWT),^{3,6,7} (Figure 1). The crystal structure of MSE at RT (monoclinic, $P2_1/c$, $a = 8.942$ Å, $b = 10.507$ Å, $c = 11.232$ Å, $\beta = 90.88^\circ$, $Z = 4$) is such that this methyl migration can occur with a minimum of atomic motion. Molecules related by the 2_1 symmetry operation are linked in stacks running parallel to the monoclinic b axis (see Figure 1). The methyl group to be transferred of one molecule is very close to the amino group of its nearest neighbor (at RT the intermolecular $N\cdots C$ distance is only 3.54 Å and the $O-C\cdots N$ angle is 147° ^{7,8}). X-ray crystal structure analyses at three different temperatures (193, 255, and 298 K)⁸ suggest considerable librational motion of the molecules about their long axes (L). A cooperative $\sim 10^\circ$ rotation of adjacent molecules in the stack would lead to a $N\cdots C$ distance less than 3 Å and to a nearly collinear approach of the reacting atoms.⁸ On this basis the chain mechanism of the MSE \rightarrow ZWT reaction was proposed (a correlated libration of molecules within a given

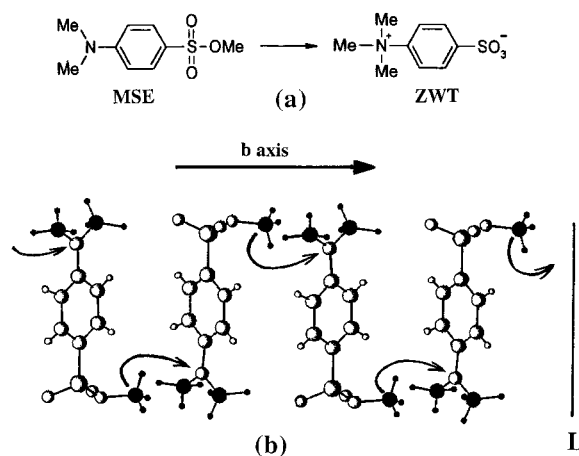


Figure 1. MSE \rightarrow ZWT solid-state thermally induced reaction. (a) Chemical equation, (b) reaction process in the crystal, where the methyl groups to be transferred are indicated by arc-shaped arrows (the b -axis is parallel to stacks of MSE molecules) and the long molecular axis L is also indicated.

chain which leads to concerted methyl transfer from molecule to molecule).^{3,7,8}

The reaction time of this rearrangement is strongly temperature dependent (about 20 days at RT, about 24 h at 323 K^{7,9,10}); the reaction rate abruptly drops at the melting point (364 K) which gives a final proof of an orientation-related acceleration of this process.⁷

Thorough calorimetric studies revealed that the DSC output curves (in both the scanning and isothermal measurements) comprise a broad maximum followed by a rather sharp (also exothermic) peak.^{10,11} This peak (which begins at conversion $\alpha_c = 60 \pm 3\%$ ¹⁰), on the basis of its sample dependent characteristics, gives evidence for a physical process (a lattice transformation) partially coincident with the chemical rearrangement;^{10,11} this conclusion was supported also by some polarized light observations and Raman scattering data.¹¹

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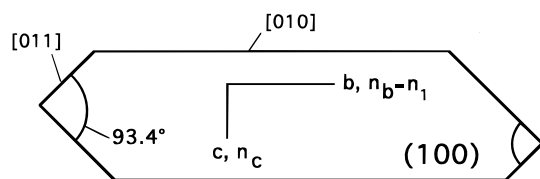


Figure 2. Drawing showing morphological and optical features of a typical very thin (100) plate of the MSE crystal. The characteristic profile angle 93.4° is the same on both sides. In the middle, both extinction directions with corresponding refractive indices, $n_b = n_1$ (the smallest principal refractive index) and n_c are shown.

Zwitterionic product has its own orthorhombic crystalline structure,^{12,13} different from the initial MSE crystal but related to it as inferred from our previous results.¹¹ This structure contains polar chains of molecules running along the c -axis ($c/L/n_3$, n_3 being the highest principal refractive index¹¹) in antiferroelectric manner.^{12,13} Rich phase transition phenomena, including ferroelasticity, occurring in ZWT crystals were recently studied.^{13,14}

Recent calculations showed that the internal energy of the isolated MSE molecule is much smaller than the one of the isolated ZWT molecule;¹⁵ but the authors found that the ZWT crystal is energetically more stable than the MSE crystal by about 71 kJ mol^{-1} .¹⁵ This value is slightly underestimated: the experimental enthalpy given by our isothermal calorimetric measurements is equal to -88 kJ mol^{-1} in the $300\text{--}360 \text{ K}$ range.¹⁶ This value is deduced from the total enthalpy of the exotherm obtained by increasing temperature (-66 kJ mol^{-1}), in agreement with the earlier results (-63 kJ mol^{-1} , the same experimental conditions¹⁰).

Optical crystallography methods¹⁷ are widely recognized as very useful in studying polymorphs and various phase transition phenomena,^{18,19} and in many cases they can yield qualitative and quantitative information that is not available in any other way.²⁰ A literature search shows that birefringence techniques were applied to follow some reactions in the crystalline state, but very occasionally and making use of only the qualitative orthoscopic method.²¹

We present in this paper the results of detailed optical crystallographic studies (in orthoscopic and conoscopic arrangements) of the course of $\text{MSE} \rightarrow \text{ZWT}$ reaction at room temperature.

Experimental Section

MSE was synthesized according to ref 7 with some modifications.¹¹ Small single crystals were grown by room temperature evaporation of a methanol solution and stored at 200 K . (Some quantitative optical characteristics to be described later could be readily used to verify that the material stored remained unreacted for many months.)

Crystal optical studies were performed using research-type polarized light microscopes equipped with numerous supporting optical accessories (such as a universal stage, tilting compensators, immersion oil objective $100\times/1.30$, and many others).

Results and Discussion

1. Crystal Optical Properties of Pure (Unreacted) MSE (RT, $\lambda = 0.59 \mu\text{m}$). Small, well-formed, colorless (100) crystal plates of MSE (thickness $10\text{--}70 \mu\text{m}$, area $0.2\text{--}2 \text{ mm}^2$) grown from a methanol solution were used. Their morphology is schematically presented in Figure 2. They were elongated parallel to the monoclinic b -axis with the characteristic profile angle of 93.4° . (This angle, calculated from X-ray single-

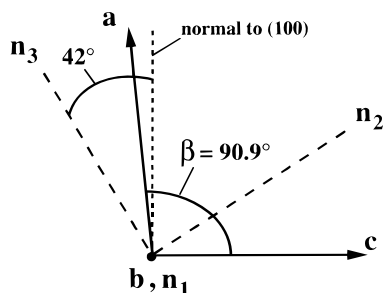


Figure 3. The indicatrix orientation within the monoclinic MSE lattice. Monoclinic angle $\beta = 90.9^\circ$.⁷

crystal diffraction data⁷, amounts to 93.8° .) It may be noted that morphological features together with parallel extinction of these plates (the extinction directions are shown in Figure 2) indicate monoclinic symmetry (point group $2/m$), in agreement with X-ray diffraction data.^{7,8}

Important information about the biaxial indicatrix (the refractive index ellipsoid constructed on the three principal indices, $n_1 < n_2 < n_3$) and its orientation within the crystal was obtained by a qualitative and quantitative analysis of the interference (conoscopic) figure given by (100) plates. In agreement with monoclinic symmetry, one of these indices, in this case n_1 , coincides with the b -axis, and the other two, n_2 and n_3 , lie in the (010) symmetry plane. The indicatrix orientation is remarkably "dictated" by the molecular arrangement within the crystal lattice. The angle between the long molecular axis L (practically corresponding to the highest molecular polarizability) and the normal to the (100) plates (calculated according to X-ray diffraction data⁸) amounts to $40 \pm 0.3^\circ$. This angle almost nearly coincides with that between the highest refractive index n_3 and the same normal: $42 \pm 1.5^\circ$ (the average value from conoscopic and orthoscopic measurements). The indicatrix orientation within the monoclinic MSE lattice is presented in Figure 3.

Markedly positive character (i.e., small optic axial angle, $(+)$ $2V = 21.1^\circ$),¹¹ with n_3 being the bisectrix of this angle) together with the refractive indices values $n_1 = 1.530$ (5), $n_2 = 1.537$ (5), and $n_3 = 1.798$ (10) additionally reflect close relation between molecular packing in the MSE crystal and its birefringent properties.

So, the two important directions in the lattice, i.e., the stack axis and the long molecular axis, are readily recognizable optically.

Until now there is no information on other anisotropic physical properties to be compared with these optical data.

2. MSE \rightarrow ZWT Reaction Course Followed Optically ($\lambda = 0.59 \mu\text{m}$). A birefringence within the (100) plane for unreacted MSE was carefully determined by counting the isochromatic curves on viewing an interference figure.^{17,18} Many samples of various thicknesses (measured optically) were used. The average value of $\Delta n_{bc} = n_c - n_b$ thus obtained amounts to 0.114 (4) and is a useful and readily measurable characteristic of the RT crystalline structure of pure MSE (Δn_{bc} calculated from the indicatrix parameters given earlier, ~ 0.11 , agrees with this value).

Noticeable changes with time of the interference colors in white light shown by very thin ($10\text{--}20 \mu\text{m}$) plates gave a first sign of distinct Δn_{bc} diminishing during the reaction. Using the tilting (Ehringhaus) compensator to somewhat thicker samples confirmed this tendency.

Careful and many times repeated measurements of Δn_{bc} vs reaction time were performed. A representative curve for isothermal measurements at $T = 293 \text{ K}$ is presented in Figure 4.

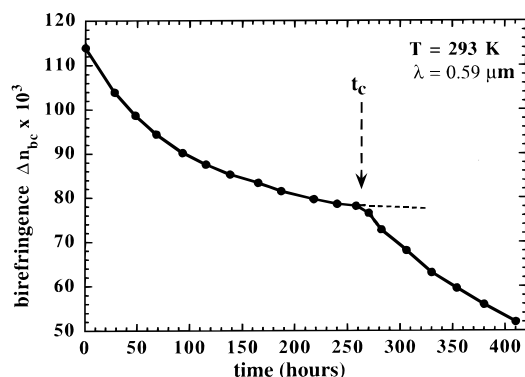


Figure 4. The birefringence Δn_{bc} vs time dependence during the MSE \rightarrow ZWT reaction course at $T = 293$ K. Anomaly (indicated by a vertical arrow) at $t_c = 266$ h corresponds to the lattice transformation.

Clear anomaly occurring at a critical time $t_c = 266$ h (indicated by a vertical arrow) corresponds to the lattice transformation at $\alpha_c \sim 0.60$ conversion (see Introduction). The birefringence Δn_{bc} at t_c , amounting to 0.077 (2), was verified to be temperature independent and is the optical characteristic of the crystalline structure at this reaction stage. Noteworthy also is a “saturation” region observed slightly below t_c , which indicates that the MSE \rightarrow ZWT rearrangement proceeds at a distinctly slower rate.

The first part (until t_c) of the Δn_{bc} curve is, for a given temperature, very reproducible: different samples, and also different regions (about 1–2 mm distant) of the same sample, showed analogous (within less than 1%) birefringence behavior. It should be noted that t_c values and sample independence of the Δn_{bc} curve are in agreement with calorimetric data¹⁰ (see also (3) in Conclusion). These findings, as well as some other optical anisotropic properties we followed orthoscopically, give a clear indication that, for $0 < \alpha < \sim 0.60$, the MSE–ZWT mixed crystals formed are optically homogeneous and highly crystalline, with the reference MSE lattice remaining approximately constant. Moreover, we verified that the indicatrix axes lying within the (010) symmetry plane suffer from very small progressive rotation (about 0.8° , as monitored conoscopically), which indicates that very probably initial monoclinic symmetry is preserved until t_c .

After t_c , the samples generally lose (but not completely) their single crystal appearance by developing at the beginning of the transformation very small (about 2–5 μm large) microcrystalline regions.¹¹ These regions (distributed very randomly) are readily noticed in the orthoscopic arrangement (particularly when a sample is placed in the extinction position, this position being unchanged from the very beginning of the reaction), and thus give an easy sign of t_c . Their number increases progressively with time, and the period of time needed to complete their development is in good correspondence with the duration of the second maximum observed in calorimetric studies (about 50–60 h at RT,¹⁰ about 25 min at $T = 339$ K¹⁶). Preferred orientation of these regions was noticed (on areas of their occurrence some birefringent properties could be observed), and this orientation was roughly like that of monocrystalline parts to be described below.

When the reaction was going at or below RT and thinner (~ 20 μm) and excellent quality MSE plates were chosen optically, rather large parts of the samples preserved their monocrystalline character (without a change of the extinction directions) after passing the lattice transformation. Such parts gave a possibility of performing quantitative measurements (both orthoscopic and conoscopic) after t_c .

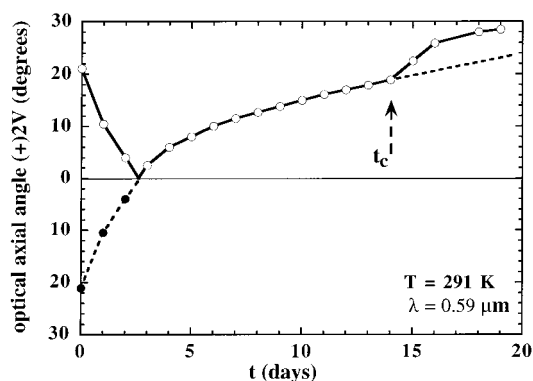


Figure 5. The optic axial angle $2V$ vs time dependence during the MSE \rightarrow ZWT reaction course at $T = 291$ K. Experimental points below time of uniaxiality are additionally presented “in reflection” (black circles), see text. Anomaly at t_c (indicated by a vertical arrow) corresponds to the lattice transformation.

Final Δn_{bc} values which could be measured for different samples varied from about 0.035 to about 0.050.

The other optical characteristic which we followed quantitatively was the optic axial angle $2V$. For this purpose thin crystalline films of pure MSE were prepared from the melt. They were, in general, optically oriented similar to solution grown (100) plates, but in some regions much more preferable orientation was found, i.e., with the bisectrix of the $2V$ angle almost perpendicular to them. A representative $2V$ vs time curve at $T = 291$ K is presented in Figure 5. This curve resembles to a great extent in character the birefringence Δn_{bc} curve (Figure 4). To make this similarity more evident, the experimental points below time of uniaxiality (to be discussed below) are additionally presented “in reflection”. Anomaly observed at the lattice transformation time t_c is marked by a vertical arrow.

In the initial reaction stage (higher reaction rate, higher $2V$ changes) spectacular crossed axial plane evolution of the indicatrix is observed. In pure MSE the optic axial plane is perpendicular to the (010) crystallographic symmetry plane, and after ca. 3 days the optic axial plane becomes parallel to the (010) plane (i.e., initially $b \parallel n_1$ becomes $b \parallel n_2$). For a while a reacting MSE sample is optically uniaxial ($n_1 = n_2$, $2V = 0$, n_3 being the optic axis). Afterward, $2V$ increases progressively to reach in the final stage of the conversion a value $(+) 2V = 27\text{--}30^\circ$ (specimen dependent). The bisectrix of $2V$ does not change practically its position during the whole reaction course. The optic axial angle for pure and highly ordered orthorhombic crystals of ZWT grown independently from a water solution amounts to $(+) 2V = 26.6$ (5) $^\circ$.¹³ Good agreement between these $2V$ values indicates that the final ZWT structure formed in situ in reacted crystals is only slightly disordered.

The MSE \rightarrow ZWT reaction on the surface proceeds more slowly than in the bulk crystal as was experimentally evidenced.^{9,10} For most of our samples, in the final reaction stages, birefringent properties could not be further observed (very likely due to minute polycrystalline product accumulated on the surface; this process was not studied here). However, some exceptions were noticed where, after many months, these properties (at least in some places of a reacted sample) were still shown.

Conclusion

Optical crystallographic methods turned out to be suitable to follow the MSE \rightarrow ZWT reaction process. Main conclusions to be inferred from this work (which are in agreement with

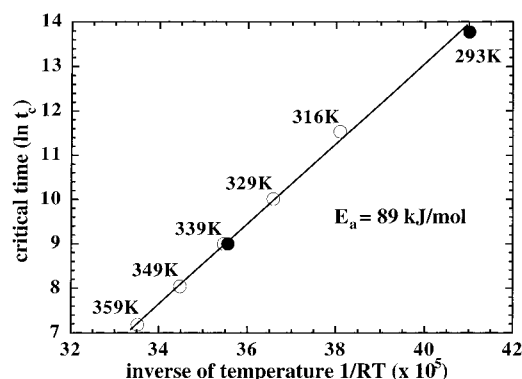


Figure 6. Logarithms of the critical times t_c of the transformation (t_c in seconds) as a function of $1/RT$ in the 293–360 K range. Open circles: our calorimetric data. Black circles: birefringence data. The straight line is a linear fit of the calorimetric and optical data and its slope corresponds to the activation energy.

general structural features of this reaction) are as follows:

(1) The MSE monoclinic lattice “stands” well, as much as ~60% of its neutral molecules being replaced by zwitterionic ones before it becomes unstable and undergoes a transformation to the orthorhombic ZWT lattice.

(2) This transformation is accompanied by clear anomalies of the birefringence Δn_{bc} and the optic axial angle $2V$.

(3) The critical times t_c of this transformation (for various temperatures) found optically are in agreement with the ones obtained by DSC calorimetry. Figure 6 shows that the logarithms of t_c values are a linear function of $1/RT$ in the 293–360 K range. A value of activation energy equal to 89 kJ mol⁻¹ is deduced from it.

(4) When the reaction proceeded at RT (or below RT) and when very thin good quality crystals were used, some parts of the samples preserved monocrystalline character after the lattice transformation.

(5) The optical indicatrix orientation during the whole reaction remains practically (within one degree) constant, the direction of the highest refractive index n_3 corresponding (both for the initial MSE lattice and finally formed ZWT lattice) to the long molecular axes.

(6) The indicatrix parameters (i.e., optical anisotropy) progressively and markedly change as a function of the reaction time (as reflected, e.g., by crossed axial plane evolution to a substantial ~48°). Optical properties of the last in situ formed ZWT lattice are in good correspondence with these properties observed in independently solution-grown ZWT crystals.

(7) A final and general remark: this work shows the utility of the optical birefringence technique to studies of solid-state reactions. Its sensitivity to structural changes and minute quantities of material it needs (in many cases samples of ~50 μ m in average diameter, i.e., much less than 1 μ g, are appropriate) suggest it to be one of the first techniques to try in investigations of new potentially reactive crystalline materials. Our currently-in-progress optical studies similar to the MSE \rightarrow ZWT reactions are in agreement with this remark.

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