

## THERMAL STABILITY OF *para*- AND *ortho*-ISOMERS OF TRIS-DECYL-(ETHYL-BENZYL)-AMMONIUM CHLORIDE

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Thermal stability of *para* (*p*-) and *ortho* (*o*-) isomers was investigated by CRTG and reaction kinetic analysis. The temperature started the mass decrease of *o*-isomer was about 20°C lower than that of *p*-isomer by CRTG. The activation energies of thermal decomposition of *o*- and *p*-isomers were 136.9 and 153.4 kJ mol<sup>-1</sup>, respectively. The effect of steric hindrance on heat of formation was calculated by AM1 method using Win MOPAC3.0 for the model compound of *p*- and *o*-isomers. The lower stability of *o*-isomer was the results of the steric hindrance between the ethylene unit of aromatic ring and three alkyl chains.

**Keywords:** CRTG, heat of formation, isomer, steric hindrance, thermal decomposition

### Introduction

We have proposed new method to prepare the structure controlled polymer from amphiphilic monomers, which formed self-assemble ordered structure on various solid surfaces [1]. Tris-decyl-(vinyl-benzyl)-ammonium chloride is one of self-assemble amphiphilic monomers, gives highly ordered polymer which consisted of stacked bilayers of amphiphilic monomer. Tris-decyl-(vinyl-benzyl)-ammonium chloride has two isomers, *para*- and *ortho*-substitutes, these isomers give different type of self-assemble bilayers and thermal stability.

Thermal stability of isomers are reported for nitrotoluene [2], nitrophenol [3], nitroaniline [4], nitrophenylhydrazine [5] and isomeric polymers [6, 7]. *Para*-isomer (*p*-isomer) is more stable than *ortho*-isomer (*o*-isomer) due to steric hindrance of *o*-isomers [4, 5, 8]. For isomeric polymers, *cis*- and *trans*-isomers show different thermal decomposition behaviors [6] and the head-head type polystyrene show less thermal stability than the head-tail type polystyrene due to the steric hindrance of intramolecular rotation [7].

Intermolecular interactions such as hydrogen bond and acid-base interactions contribute to increase thermal stability of molecules [9, 10]. Amphiphilic molecule, tris-decyl-(vinyl-benzyl)-ammonium chloride, contained both intra- and intermolecular interactions and steric hindrance caused by three alkyl chains. In this study, the thermal stability of isomers having long alkyl chains was investigated by kinetic analysis of thermal decomposition, controlled rate thermogravimetry (CRTG) and molecular orbital calculation.

### Experimental

#### Samples

Two types of tris-decyl-(ethyl-benzyl)-ammonium chloride were used as the model compound of tris-decyl-(vinyl-benzyl)-ammonium chloride monomer. Tris-decyl-(4-ethyl-benzyl)-ammonium chloride (*p*-isomer) and tris-decyl-(ethyl-benzyl)-ammonium chloride which contained 10 mol% of tris-decyl-(2-ethyl-benzyl)-ammonium chloride (*o*-isomer) were used through the experiments.

#### Preparation of 1-chloromethyl-4-ethyl-benzene (1)

An amount of 5.382 g ( $4.5 \cdot 10^{-2}$  mol) of thionyl chloride was solved in 10 mL of dry benzene. A few drops of pyridine were added as catalytic agent. An amount of 5.142 g ( $3.8 \cdot 10^{-2}$  mol) of (4-ethyl-phenyl)-methanol solved in 15 mL of dry benzene was cautiously dropped into benzene solution of thionyl chloride with dropping funnel. This solution was stirred for 1 h at 60°C under nitrogen atmosphere. The combined solution and thionyl chloride were evaporated and the obtained residue was purified by short silica gel column chromatograph with acetic acid as the eluent to yield 1-chloromethyl-4-ethyl-benzene as light yellow liquid. The yield was 72% (4.2 g).

#### Preparation of tri-decyl-(4-ethyl-benzyl)-ammonium chloride (2)

An amount of 4.2 g ( $2.7 \cdot 10^{-2}$  mol) of **1** and 4.3783 g ( $1.0 \cdot 10^{-2}$  mol) of tri-*n*-decylamine was solved in

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100 mL of dichloromethane. This solution was stirred for 2 days at room temperature. The combined solution was evaporated and the obtained residue was purified by silica gel column chromatograph with acetic acid as the eluent to get rid of impurity. The 1.5 cm silica gel from original point was stirred with methanol. Tris-decyl-(4-ethyl-benzyl)-ammonium chloride, *p*-isomer was extracted, the yield was 61% (3.2 g).

*p*-isomer;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS, d, ppm),  $\delta$  7.43 (d, 2H, Ar), 7.27 (d, 2H, Ar), 4.89 (s, 2H,  $\text{CH}_2\text{N}$ ), 3.31 (t, 6H, N ( $\text{CH}_2$ )<sub>3</sub>), 2.72 (f, 2H,  $\text{ArCH}_2\text{CH}_3$ ), 1.75 (f, 6H, N ( $\text{CH}_2\text{CH}_2$ )<sub>3</sub>), 1.32 (f, 42H,  $\text{CH}_2\text{CH}_3$ ), 1.30 (t, 3H,  $\text{CH}_3\text{CH}_2\text{Ar}$ ), 0.90 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), *o*-isomer  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS, d, ppm),  $\delta$  7.6–7.4 (d, 4H, Ar), 4.92 (s, 2H,  $\text{CH}_2\text{N}$ ), 3.48 (t, 6H, N ( $\text{CH}_2$ )<sub>3</sub>), 2.80 (f, 2H,  $\text{ArCH}_2\text{CH}_3$ ), 1.76 (f, 6H, N ( $\text{CH}_2\text{CH}_2$ )<sub>3</sub>), 1.33 (f, 42H,  $\text{CH}_2\text{CH}_3$ ), 1.31 (t, 3H,  $\text{CH}_3\text{CH}_2\text{Ar}$ ), 0.92 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).

1-chloromethyl-4-ethyl-benzene purchased from Tokyo Kashei, which contained about 3% of 1-chloromethyl-2-ethyl-benzene was used instead of **1** for the preparation of **2**. The obtained tris-decyl-(ethyl-benzyl)-ammonium chloride contained about 10 mol% of *o*-isomer, was used as the mixture of *p*- and *o*-isomers (*p*-*o* mixture) from  $^1\text{H-NMR}$  measurement.

## Methods

### CRTG experiments

Thermal stability of samples was investigated by CRTG measurement by a Seiko Instrument TG/DTA 6200. Sample mass of *p*-*o* mixture and *p*-isomer were about 4 and 2 mg, respectively. Measurements were

performed at  $10^\circ\text{C min}^{-1}$  in nitrogen atmosphere at  $40 \text{ mL min}^{-1}$  gas flow. The decrease rate of mass was controlled at  $5.5 \pm 0.5 \mu\text{g min}^{-1}$ . Aluminum crucibles with caps pitted a small hole were used.

### NMR experiments

$^1\text{H-NMR}$  measurement was carried out for the determination of decomposed compounds. The *p*-isomers annealed at 100, 110 and  $120^\circ\text{C}$  for various periods from 30 to 120 min, and *p*-*o* mixture annealed at 95, 100 and  $105^\circ\text{C}$  for various periods from 3 to 90 min in the closed aluminum crucibles using TG/DTA 6200 were used for NMR experiments. After annealing under various conditions, the annealed samples were dissolved in  $\text{CHCl}_3$ , and were investigated by  $^1\text{H-NMR}$  JEOL EX270 (270 MHz).

### Molecular orbital calculations

Molecular orbital calculation was performed by AM1 method using Win MOPAC3.0 for tri-ethyl-(4-ethyl-benzyl)-ammonium chloride and tri-ethyl-(2-ethyl-benzyl)-ammonium chloride as the model compounds of *o*-isomer and *p*-isomer, respectively. The parameters used for the calculation were AM1, GEO-OK, PRECISE, GNORM=0.1 and CHARGE=1. The obtained results were checked by FORCE calculation in order to confirm the grand state.

## Results and discussion

CRTG curves of mixture and *p*-isomer were shown in Fig. 1. CRTG curve of *p*-*o* mixture showed two steps

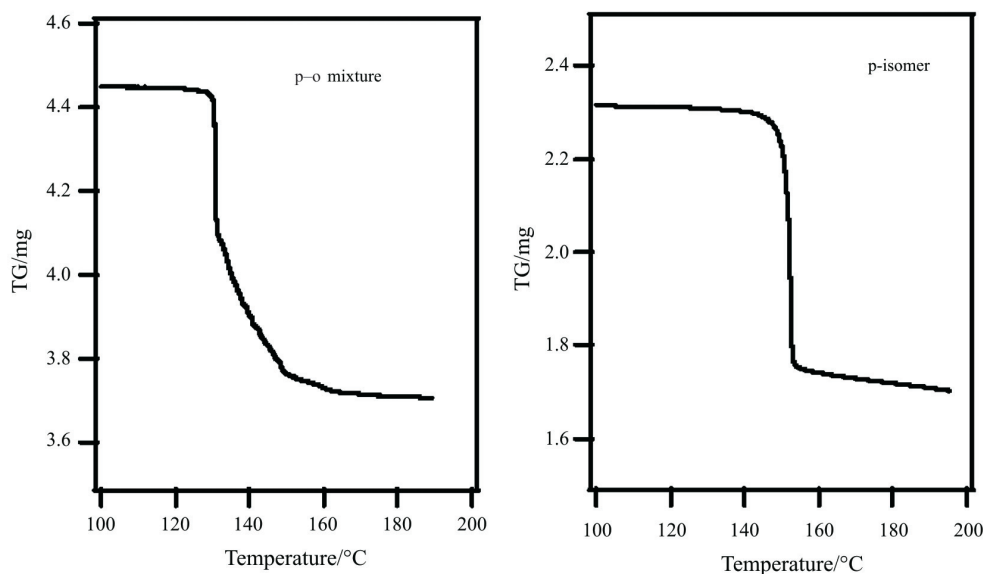
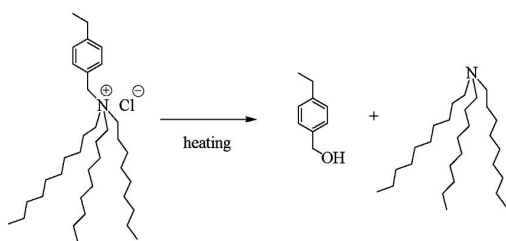


Fig. 1 CRTG curves of *p*-*o* mixture and *p*-isomer obtained at  $5\text{--}6 \text{ mg min}^{-1}$



Scheme 1

mass decreases, the first decrease occurred isothermally and the second decrease occurred continuously. On the other hand the mass loss of *p*-isomer occurred isothermally at a single step. The mass loss at 180°C of *p*-*o* mixture and *p*-isomer were 21.4 and 23.9%, respectively. These mass loss values indicated that (4-ethyl-phenyl) methanol and chloride evaporated as decomposed compounds. The mass decrease of *p*-*o* mixture started at 130°C, which was about 20°C lower than *p*-isomer. These results suggested that *o*-isomer decomposed at lower temperature than *p*-isomer. Thermal stability of *p*-isomer was higher than that of *o*-isomer.

The decomposed compounds were analyzed by <sup>1</sup>H-NMR. The methylene unit connected with nitrogen atom showed NMR peak at 4.89 ppm for *p*-isomer and 4.92 ppm for *o*-isomer, however, the decomposed compound had the peaks at 4.54 and 4.64 ppm which were assigned to the methylene unit connected to hydroxyl group for *p*- and *o*-isomers, respectively. This result suggested that tris-decyl-(ethyl-benzyl)-ammonium chloride decomposed by the cleaving C–H linkage between ammonium and methylene units. The thermal decomposition reaction of tris-decyl-(ethyl-benzyl)-ammonium chloride was expected as shown in Scheme 1, which showed a good agreement with the result of mass loss obtained by CRTG.

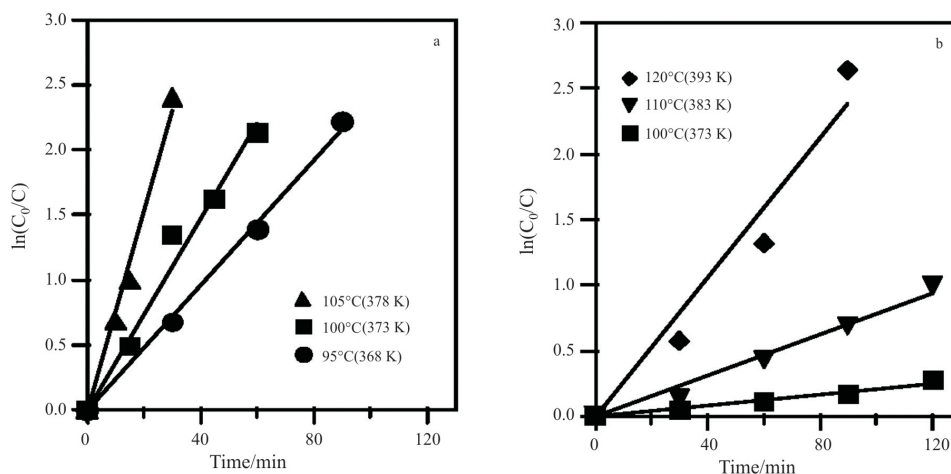
The peak areas of NMR peak at 4.89 and 4.54 ppm indicated the total amounts of un-decomposed and decomposed compounds, respectively. By assuming the first order reaction, the reaction rate constant of thermal decomposition was described by Eq. (1).

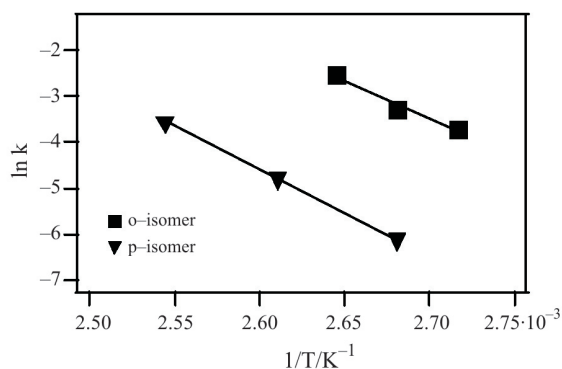
$$\ln\left(\frac{A_{p,o} + A_{deco}}{A_{p,o}}\right) = \ln\left(\frac{C_0}{C}\right) = kt \quad (1)$$

Here,  $A_{p,o}$ ; peak area of NMR peak at 4.89 ppm (*p*-isomer) and 4.92 ppm (*o*-isomer),  $A_{deco}$ ; peak area of NMR peak at 4.54 ppm (decomposition compound from *p*-isomer) and 4.64 ppm (decomposition compound from *o*-isomer),  $C_0$ ; initial concentration of *p*- and *o*-isomers,  $C$  concentration of *p*- and *o*-isomers annealed for time annealing  $t$ ;  $k$ ; reaction rate constant.

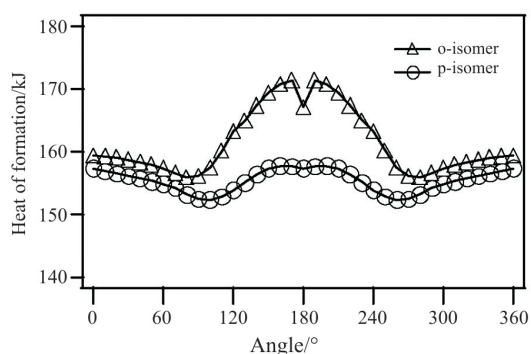
The relationship between  $\ln(C_0/C)$  and  $t$  at various decomposition temperatures for *p*-*o* mixture and *p*-isomer was shown in Fig. 2. The plots of  $\ln(C_0/C)$  vs.  $t$  showed a good linear relationship at each temperature. The reaction rate constants ( $k$ ) calculated from the slope of linear relationship in Fig. 2 was plotted vs. the reciprocal temperature in Fig. 3. The reaction rate constant ( $k$ ) of *o*-isomer was larger than that of *p*-isomer at same temperature. It was indicated that *o*-isomer was decomposed faster than *p*-isomer. This result agreed with the CRTG results, in which *o*-isomer decomposed at lower temperature than *p*-isomer. From Arrhenius plot of  $\ln k$  shown in Fig. 3, the activation energies of decomposition for *o*- and *p*-isomers were evaluated. The obtained activation energies of *o*- and *p*-isomers were 136.9 and 153.4 kJ mol<sup>-1</sup>, respectively. These results also suggested that *o*-isomer decomposed at lower temperature and faster than *p*-isomer as indicating in CRTG experiment.

The thermal stability of isomers is well described by the effect of steric hindrance of molecules [2–5]. The molecular orbital calculation is powerful method

Fig. 2 Decomposition rate plots of a – *p*-*o* mixture and b – *p* – isomer



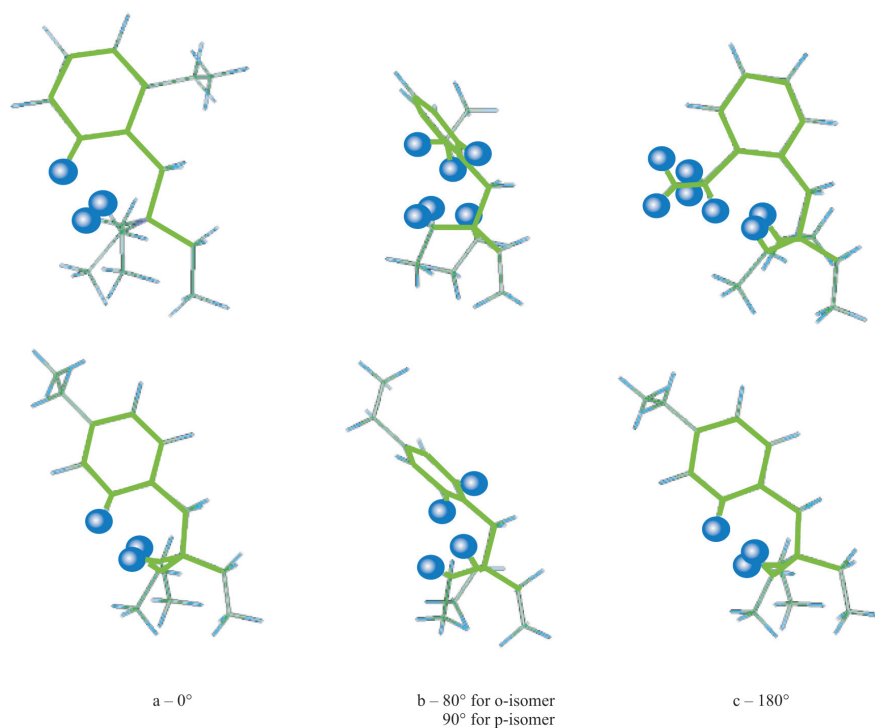
**Fig. 3** Arrhenius plots of  $\ln k$  for *o*- and *p*-isomers



**Fig. 4** Changes of heat of formation as a function of the angle between N–C–C plane and aromatic ring calculated semi-empirical AM1 method

to estimate the heat of formation as a function of molecular conformation. The steric effect on pyrene pyrolysis is investigated by the conformational calculation using AM1 method [11]. The heat of formation was calculated by AM1 method (WinMOPAC) as a function of the angle between aromatic ring and the plane of N–C–C linkage for the model compound of *p*- and *o*-isomers. The calculated heat of formation was shown in Fig. 4 as a function of the angle between two planes formed by aromatic ring and N–C–C linkage for *p*- and *o*-isomers. The changes of heat of formation for *o*-isomer differed from that of *p*-isomer. The minimum values were obtained at 90 and 270° for *p*-isomer and at 80 and 280° for *o*-isomer, and the heat of formation at the minimum of *o*-isomer was larger than that of *p*-isomer. These minimum values gave the stable conformation of *o*- and *p*-isomers. The difference between *o*- and *p*-isomers was due to the steric hindrance between the ethylene unit connected to aromatic ring and three alkyl chains (ethylene unit in model compound) connected to nitrogen.

The conformational structures of *o*- and *p*-isomers at various angles between two planes formed by aromatic ring and N–C–C linkage were shown in Fig. 5. Both *o*-isomer and *p*-isomer were slightly unstable at 0° due to steric hindrance between hydrogen atoms belonged to aromatic ring and one of three alkyl chains connected to nitrogen atom. The most stable conformation was obtained at 80 and 90° for



**Fig. 5** Structures of *o*-isomer and *p*-isomer at various angle between N–C–C plane and aromatic ring. a – 0°, b – 80° for *o*-isomer, 90° for *p*-isomer, c – 180°

*o*-isomer and *p*-isomer, respectively, and gave the lowest heat of formation. In these stable conformations, hydrogen atoms belonged to aromatic ring were far away from alkyl chains connected with nitrogen. As the conformation of *p*-isomers at 180° was same to the conformation at 0°, the value of heat of formation for *p*-isomers at 180 and 0° were the same. However, the heat of formation of *o*-isomer in the range of angle between 120 and 180° was larger than that of *p*-isomers, because the steric hindrance between the ethylene unit connected to aromatic ring and three alkyl chains (ethylene unit in model compound) connected to nitrogen. The conformation of *o*-isomer at 180° scarcely realized because the ethylene unit of aromatic ring overlapped on one of three alkyl chains. With increasing thermal motion of *o*-isomer, three alkyl chains connected to nitrogen atom rotated freely, however, the ethylene unit of *o*-isomer disturbed to form the stable conformation. Hence, *o*-isomer decomposed faster than *p*-isomer due to the steric hindrance between ethylene unit and three alkyl chains.

## Conclusions

Thermal stability of *p*- and *o*-isomers of tri-decyl-(ethyl-benzyl)-ammonium chloride was investigated by CRTG and the reaction kinetics. The rate constant of thermal decomposition of *o*-isomer was 10<sup>3</sup> times larger than *p*-isomer at a fixed temperature. The activation energy of thermal decomposition of *o*- and *p*-isomers were 136.9 and 153.4 kJ mol<sup>-1</sup>, respectively.

The heats of formation at various conformation as a function of rotating angle between aromatic ring

and C–C–N plane was calculated by AM1 method (Win MOPAC) for the model compounds of *o*-isomer and *p*-isomer replacing three long alkyl chains to three ethyl chains. The stable conformation of *o*- and *p*-isomers was obtained at 80 and 90°, at the angle range above 90° the heat of formation of *o*-isomer became larger than *p*-isomer. The increase of heat of formation caused the lower thermal stability of *o*-isomer. The experimental and calculated results indicated the lower thermal stability of *o*-isomer due to the steric hindrance between the ethylene unit connected to aromatic ring and three alkyl chains.

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DOI: 10.1007/s10973-006-7661-8