Thermodynamic and kinetic studies on *R*(+) and *S*(-)-2,2'-dihydroxy-1-, 1'-binaphthyls in solid state

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Many organic reactions[1)] can be carried out in the absence of solvent and many solid state reactions proceed more selectively than reactions in solution. When powdered *R*(+)- and *S*(-)-2,2'-dihydroxy-1-,1'-binaphthyl's crystals were mixed in solid state, the crystal of the *racemic*-2,2'-dihydroxy-1-,1'-binaphthyls were formed.[2-6)] In order to understand reaction kinetics and mechanism of the reaction, *R*(+)-, *S*(-)- and *racemic*-2,2'-dihydroxy-1-,1'-binaphthyl's crystal have been studied by solution calorimetry and thermal analysis.

Calorimetric measurements were carried out on isoperibol and isothermal solution calorimeter (LKB2225 and LKB 2222 Thermal Activity Monitor, Thermometric AB Järfälla, Sweden) at (298.15±0.0001) K and (298.15±0.0001) K, and differential scanning calorimeter TG-DTA-MS (Rigaku, TG8101), DSC (Rigaku, DSC8270A, DSC8240D)

The phase diagram of *R*(+)- and *S*(-)-2,2'-dihydroxy-1-,1'-binaphthylwere determined by DSC. *R*(+)- and *S*(-)-2,2'-dihydroxy-1-,1'-binaphthyl system was simple phase diagram which showed *racemic* compound.

Enthalpy diagram of *R*(+)-, *S*(-)- and *racemic*-2,2'-dihydroxy-1-,1'-binaphthyl's crystals were determined by solution calorimetry at 298.15 K. Concentration dependence on enthalpies of solution was fitted by equation (1).

$$\Delta_{soln}H/\ \text{kJ mol}^{-1} = a + bx \qquad (1)$$

here x is mole fraction of 2,2'-dihydroxy-1,1'-binaphthyl in benzene solution. Enthalpies of solution at infinite dilution might be obtained as the parameter a in equation(1). Enthalpies of solution at infinite dilution of *R*(+)-, *S*(-)-, 2,2'-dihydroxy-1,1'-binaphthyls were(21.84±0.20) kJ mol^{-1} and (21.87±0.24)kJ mol^{-1}, respectively. Enthalpies of solution of both enantiomers were agreed with in the experimental error. Enthalpies of solution of *racemic*-2,2'-dihydroxy-1,1'-binaphthyl were (24.55±0.28) kJ mol^{-1} . An enthalpy scheme of 2,2'-dihydroxy-1,1'-binaphthyl determined showed in Fig. 1. *Rracemic*-2,2'-dihydroxy-1,1'-binaphtyl was 2.69 kJ mol^{-1} stable than *R*(+)- and *S*(-)-2,2'-dihydroxy-1,1'-binaphthyl.

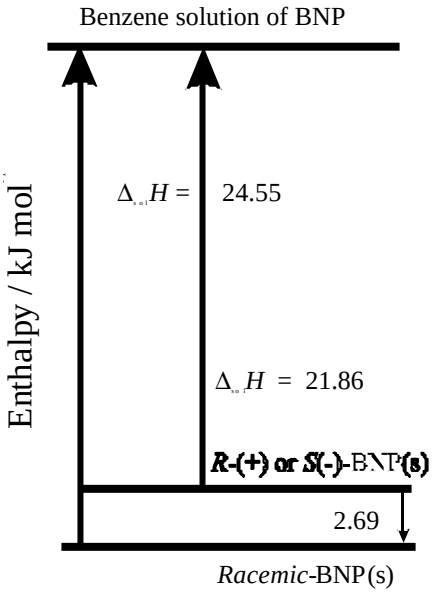

Fig. 1 Enthalpy diagram of 2,2'-dihydroxy-1,1'-binaphthyl

The reaction thermograms of mixing powdered *R*(+)- and *S*(-)-2,2'-dihydroxy-1-,1'-binaphthyl's crystals were measured. An example of reaction thermograms was shown in Fig. 2 and 3. The reaction thermograms of mixing powdere of *R*(+)- and *S*(-)-2,2'-dihydroxy-1,1'-binaphthyl were exothermic but very small changes. The formation of *racemic* crystals from enantiomer crystals was measured by different ambientes. The thermograms showed *racemic* host compound crystals by mixing two enantiomer crystals in solid state were formed very slowly. The thermograms showed *racemic* host compound crystals by mixing two enantiomer crystals in solid state were formed very slowly. Thermal power dq/dt of the reaction was analyzed by equation (2) to determined reaction rate k and reaction enthalpy ΔH.

$$\frac{dq}{dt} = P = \frac{d(\Delta n \cdot \Delta H)}{dt} = \frac{d\Delta n}{dt}\Delta H = k[S]\Delta H \qquad (2)$$

Reaction thermogram of powdered *R*(+)-, and *S*(-)-2,2'-dihydroxy-1,1'-binaphthyl and with liquid parafine[2)], water or etc. have been also measured by microcalorimetry at 298.15 K and 310.15 K. Raction schem of *R*(+)-, and *S*(-)-2,2'-dihydroxy-1,1'-binaphthyls with liquid parafine, water or etc. showed different thermal profiles as shown in Fig. 2 and Fig. 3 compared with the reaction without any liquid. Some reactions were endothermic but others were exothermic. Specailly the reaction of *R*(+)-, and *S*(-)-2,2'-dihydroxy-1,1'-binaphthyls with water showed unique rection than others.

Kinetic parameters were determined by first order reaction(3) or Ng equation(4).

$$dx/dt = A_0 k\left(1 - x/A_0\right) \qquad (3)$$

$$dx/dt = A_0 k\left(x/A_0\right)^n\left(1 - x/A_0\right)^m \qquad (4)$$

Thermoprofiles of reaction with liquids were extremly diffrent than without liquids. It might be shown diffrent reaction mechanisum between *R*(+)-, and *S*(-)-2,2'-dihydroxy-1,1'-binaphthyls. Enthalpic Enthalpies of melting and enthalpies solution of *R*(+)-, or *S*(-)-2,2'-dihydroxy-1,1'-binaphthyl showed time dependence after grand solid. In ordere to understand the mechanisum, Avrami-Erofee's equation was applied to analyse the behaviours. Thermodynamic behavour, reaction rate and mechanism of *R*(+)-, *S*(-)- and *racemic*-2,2'-dihydroxy-1-,1'-binaphthyl's crystals will be discussed.

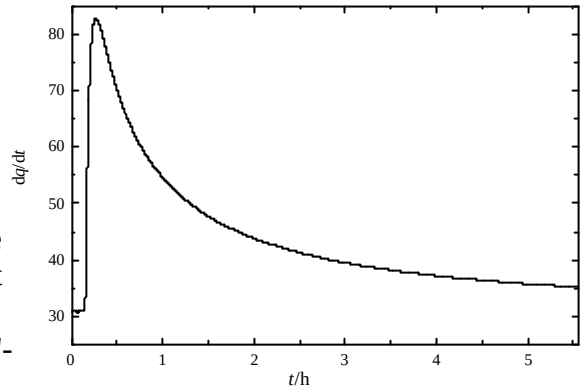

Fig.2 An Example of reaction thermogram in solid of *R*(+)-, and *S*(-)-2,2'-dihydroxy-1,1'-binaphthyl with water at 298.15 K.

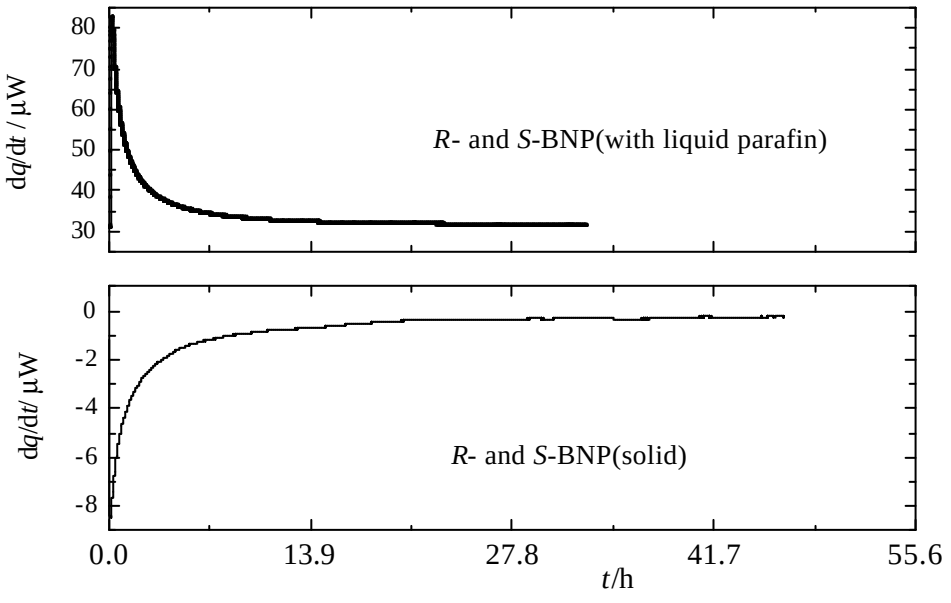

Fig. 3 An Example of reaction thermogram in solid of *R*(+)-, and *S*(-)-2,2'-dihydroxy-1,1'-binaphthyl at 298.15 K

References

1) F. Toda, *Synlett.*, **5**, 303(199.); *Acc. Chem. Res*., **28**, 480(1995).

2) F. Toda, K. Tanaka, H. Miyamoto, H. Koshima, I. Miyahara, K. Hirotsu, *J. Chem. Soc., Perkin Trans.*, **1997**,1977(1997).

3) K. Mori,Y. Masuda, S. Kashino *Acta Crystall.* **C49**, 1224(1993).

4) M. A. Didi, A. K. Maki, M. M. Mostafa, *Spectrochimica Acta*, **47A**, 667(1991).

5) T. Fujiwara, N. Tanaka, R. Ooshita, R. Hino, K. Mori, F. Toda, *Bull. Chem*. *Soc. Jpn*., **63**,249 (1990).

6) F. Toda, Y. Tagami, Q. Hao, H. Fan, T. Mak, *Chem*. *Lett*. **11**,1913 (1986).