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ENTHALPIMETRIC MEASUREMENTS IN SOLID–SOLID REACTIONS. THE FORMATION OF INTERMOLECULAR CHARGE-TRANSFER COMPLEXES

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ABSTRACT

The possibility of obtaining thermodynamic parameters from solid–solid interaction reactions in the formation of charge-transfer (CT) complexes has been studied carrying out the syntheses directly in a DSC apparatus. The interactions between the donor *p*-bromophenol and the acceptors *p*-benzoquinone, chloranyl and bromanyl have been considered. It was observed that the solid–solid interaction occurs only for the system *p*-bromophenol:*p*-benzoquinone; for the system *p*-bromophenol:bromanyl the reaction occurs in the molten donor; the acceptor chloranyl does not react.

INTRODUCTION

Considering the usefulness of solid–solid reactions for the preparation of complexes, in a previous work we have studied the possibility of obtaining thermodynamic parameters from thermoanalytical curves, carrying out the syntheses directly in a thermoanalyzer by introducing stoichiometric mixtures of the reactants into the crucible. The enthalpy changes of complex formation were calculated[1].

In this work we study the possibility of obtaining organic charge-transfer complexes (CT complexes) by solid–solid interaction, observing the reactions by DSC. Here, we report the thermodynamic parameters for the solid–solid interaction between *p*-benzoquinone and *p*-bromophenol; chloranyl and *p*-bromophenol; bromanyl and *p*-bromophenol. Each system was studied in the stoichiometric ratios (1:1), (2:1) and (1:2) of the reactants.

We have chosen these reactant systems because the difficulty of obtaining solid CT complexes is well known, and their thermodynamic parameters in solution are influenced by the solvent that is generally competitive in the donor–acceptor reaction[2, 3].

EXPERIMENTAL

Reactants

p-Bromophenol (C. Erba RP) (m.p.63–65 °C), chloranyl (Schuchardt) (m.p.295–296 °C), bromanyl (Schuchardt) (m.p.292–295 °C), and *p*-benzoquinone (Schuchardt) (m.p.115 °C) were recrystallized several times before use.

DSC measurements

All measurements were performed with a Perkin-Elmer DSC model 1B in aluminium-covered pans, in a dynamic nitrogen atmosphere ($5\ l\ h^{-1}$) at a heating rate of $4°C\ min^{-1}$.

The reactions were performed by introducing finely powdered stoichiometric mixtures of the reactants into the pan, the total weight of the system being about 5–6 mg. The empty pan was used as a reference.

The ΔH concerning the reactions was evaluated using ΔH melting of indium as calibration standard ($6.79\ cal\ g^{-1}$). All the ΔH values are reported in $kcal\ mole^{-1}$ and the molecular weight of the mixtures was calculated as if all the CT complexes (1:1; 1:2; 2:1) were already formed. These same systems were also analyzed by a Kofler apparatus to observe variation of colour, melting or decomposition during the reactions.

IR spectra (4000–$625\ cm^{-1}$)

These were performed with a Perkin-Elmer 257 spectrophotometer using KBr pellets or nujol mulls between NaCl plates.

RESULTS AND DISCUSSION

Before considering the synthesis reactions, DSC measurements were performed for all the unmixed reactants and it was observed that they are stable at the melting or decomposition temperature. Particularly, (a) *p*-bromophenol melts at 63–65 °C and then boils at 140 °C; (b) chloranyl melts with decomposition at 295–296 °C; (c) bromanyl sublimes at 292–295 °C; (d) *p*-benzoquinone sublimes at 115 °C.

Thermal syntheses

Chloranyl:p-bromophenol system. In the molar ratio 1:1, the DSC analysis, in the range 25–300 °C, exhibits two endothermic effects, respectively, at 65 °C ($\Delta H = 4.16\ kcal\ mole^{-1}$) and 295 °C, and an endo–exothermic effect in the range 220–245 °C, in which the T_m-values are 238 and 240 °C for the endothermic and exothermic effects respectively (Fig. 1).

It is noteworthy that the T_m-values of the three endothermic peaks coincide with the melting and boiling points of the *p*-bromophenol and with the decomposition temperature of the chloranyl, respectively.

In both the molar ratios 1:2 and 2:1, neither qualitative nor quantitative

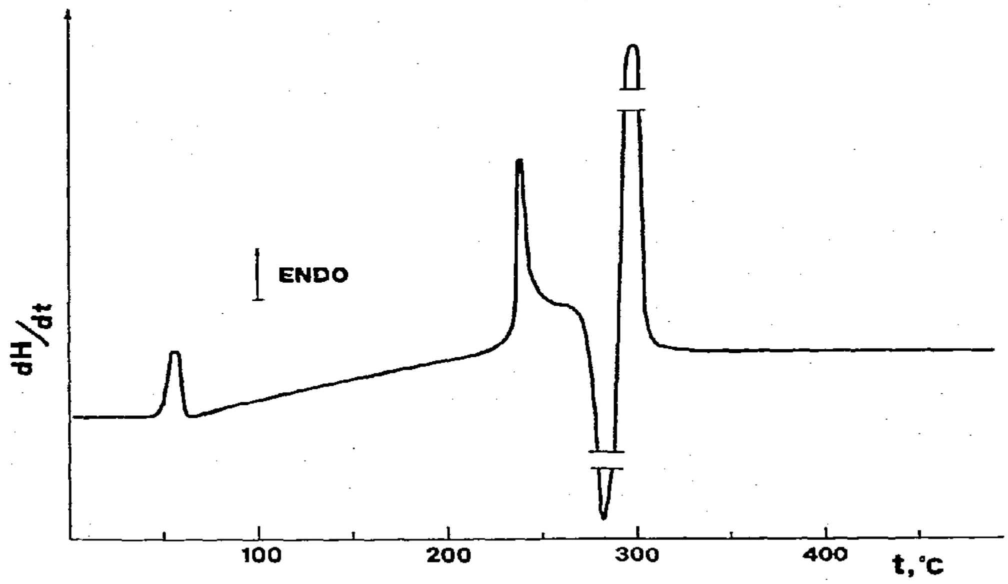

Fig. 1. Chloranyl:p-bromophenol system in the molar ratio 1:1.

differences were observed with respect to the 1:1 system. The ΔH of the first peak of the 1:2 mixture is 8.3 kcal mole^{-1} and is due to the melting of two moles of the D reactant of the mixture.

The molten mixtures 1:1, 1:2, 2:1, obtained at 70°C, were solidified by cooling and the IR spectra were performed in KBr pellets. It is possible to note that the stretching vibration at 3340 cm^{-1} of –OH of the p-bromophenol is practically invariate in the spectra of the mixtures. Therefore it is reasonable to suppose that, in the 1:1, 1:2, 2:1 mixtures of this system, the donor melts and dissolves the acceptor (the ΔH of solution being negligible) but no CT complex is formed; the exothermic effect that appears in the range 220–245°C may be due to the solidification process of the chloranyl ensuing from the boiling of the p-bromophenol.

The analysis performed with a Kofler apparatus confirms this hypothesis: at 65°C the mixture melts and no variation of colour is observed; at 238°C the molten p-bromophenol boils, evolves from the mixture and, simultaneously, the chloranyl solidifies; at 295°C the chloranyl decomposes.

Bromanyl: p-bromophenol system. In all the molar ratios considered (1:1, 1:2, 2:1), the DSC curve in the range 25–300°C exhibits first an endothermic peak (T_m = 62°C) and then an exothermic peak near 280°C, with escape of the product from the pan (Fig. 2); the temperature of this latter phenomenon is not reproducible. The molten mixtures were cooled from 80 to 25°C at 4°C min^{-1}, but no solidification was observed.

The analyses performed with a Kofler apparatus showed that, at 62–65°C, the yellow 1:1, 1:2 and 2:1 systems melt and turn red. The ΔH of the endothermic peak is 3.1 kcal mole^{-1} for the 1:1 system; 2.7 kcal mole^{-1} for the 2:1 system and 7.7 kcal mole^{-1} for the 1:2 system.

Considering that the molten p-bromophenol solidifies on cooling, it is reason-

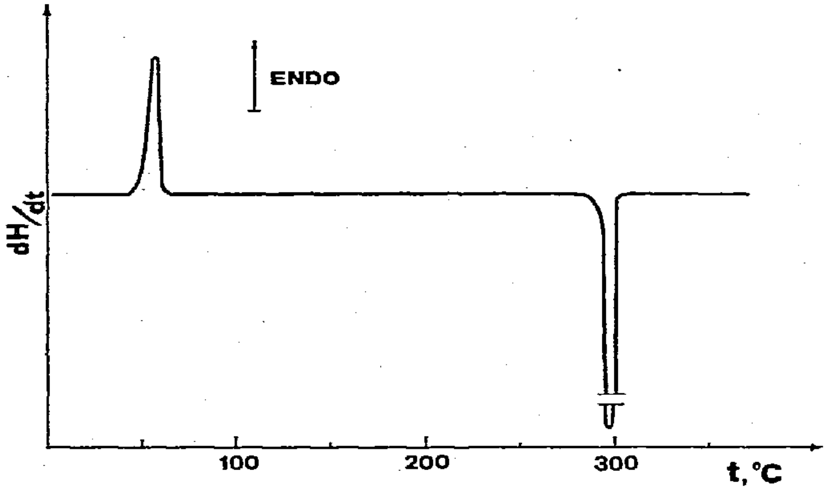

Fig. 2. Bromanyl:*p*-bromophenol system in the molar ratio 1:1.

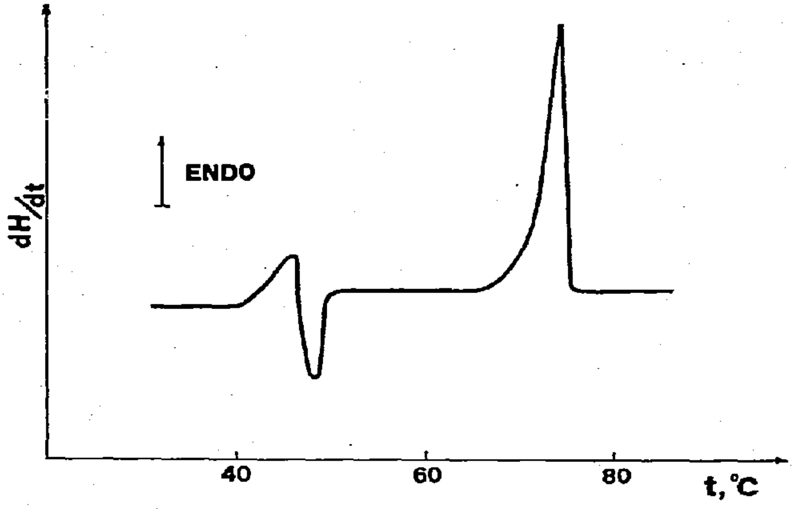

Fig. 3. *p*-Benzoquinone:*p*-bromophenol system in the molar ratio 1:1.

able to suppose that the endothermic peak is due to the sum of three simultaneous processes: the melting of the donor *p*-bromophenol, the solubilization of solid bromanyl A in molten D, the formation of CT complexes AD, AD_2, A_2D.

Considering the thermal effect due to the solubilization of A in molten D to be negligible (by comparison with the case of the chloranyl: *p*-bromophenol mixtures), the ΔH_{CT} of the complex CT formation can be calculated by the relation

$$\Delta H_{\mathrm{CT}} = \Delta H_{\mathrm{Tot}} - \Delta H_{\mathrm{melt}}$$

The IR spectra of the red liquid complexes, in NaCl plates, indicate that the ν_{OH} of the *p*-bromophenol (3340 cm^{-1}) is shifted at 3280 cm^{-1} due to the formation of a hydrogen bond.

p-Benzoquinone:p-bromophenol system. In the molar ratio 1:1, the DSC curve

(Fig. 3) shows, in the temperature range 48–51 °C, a thermal process in which an endothermic peak is followed by an exothermic one before its completion. At 74 °C the DSC curve shows an endothermic peak. The mixture is thermally stable up to 300 °C and then decomposes. If cooling takes place before reaching 300 °C, an exothermic peak at 65 °C is observed. On reheating, the DSC curve exhibits only an endothermic peak at 74 °C, thus indicating that the thermal process at 48–51 °C is due to the solid–solid interaction with formation of the solid AD complex which melts at 74 °C (ΔH = 9.5 kcal mole^{-1}). The analysis performed with a Kofler apparatus confirms this hypothesis: the yellow 1:1 mixture turns red at 48–51 °C and melts at 72–74 °C.

We think that the endo–exothermic peak at 48–51 °C can be explained by considering that the formation of the AD complex can involve some rearrangements with the formation of a polymeric structure; polynuclear molecular quinidronic complexes at the solid state are reported in the literature[4, 5].

The IR spectra of the AD complex obtained were prepared. The –OH stretching vibration of the *p*-bromophenol at 3340 cm^{-1} is shifted to 3200 cm^{-1} in this complex, clearly indicating a hydrogen bond between the –OH group and the quinonic carbonyl, peculiar to these complexes at solid state[6].

In the molar ratio 2:1 the DSC curve (Fig. 4) first shows an exothermic peak at 48 °C (ΔH = -0.6 kcal mole^{-1}) and then an endothermic peak at 71 °C (ΔH = 13.1 kcal mole^{-1}). On cooling the system from 100 to 25 °C and reheating, only the endothermic peak at 71 °C is observed (ΔH = 13.1 kcal mole^{-1}). The analysis with the Kofler apparatus shows that the yellow 2:1 mixture turns red at 48 °C and melts at 71 °C.

Therefore we think that the exothermic process at 51 °C is due to the solid–solid interaction reaction with formation of the A_2D complex, unreported in the literature. The IR spectra of the A_2D complex confirms this hypothesis, and a shift of

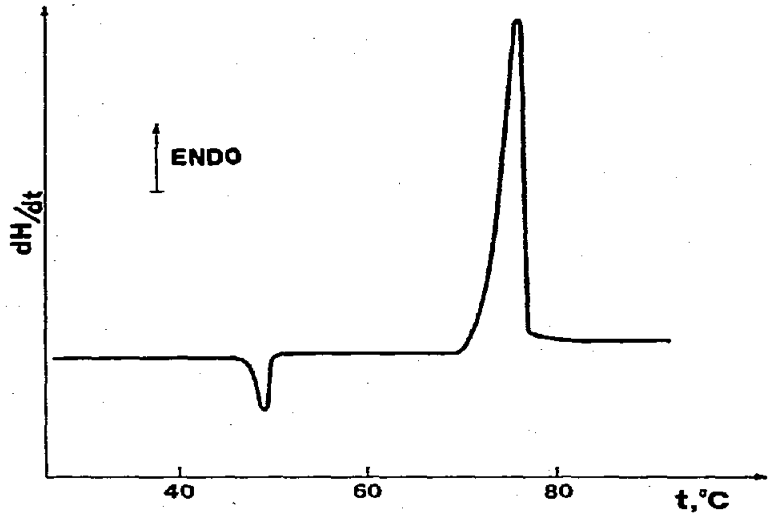

Fig. 4. *p*-Benzoquinone:*p*-bromophenol system in the molar ratio 2:1.

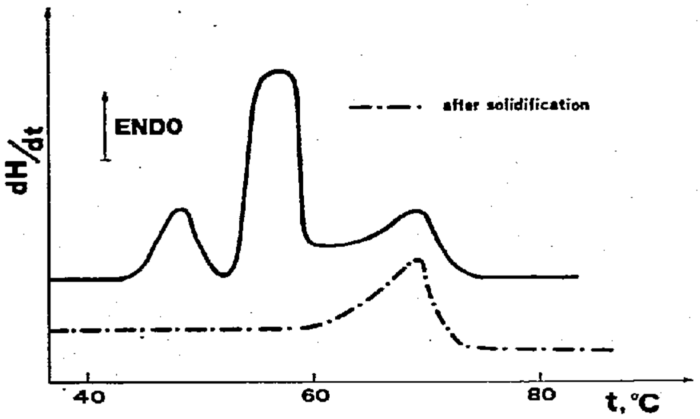

Fig. 5. *p*-Benzoquinone:*p*-bromophenol system in the molar ratio 1:2.

the –OH stretching vibration from 3340 in the *p*-bromophenol to 3230 cm^{-1} in the A_2D complex is observed.

In the molar ratio 1:2, the DSC curve (Fig. 5) in the range 25–100 °C exhibits three endothermic peaks, respectively, at 46 °C (ΔH = 0.9 kcal $mole^{-1}$), 52 °C (ΔH = 10.6 kcal $mole^{-1}$) and 67 °C (ΔH = 4.2 kcal $mole^{-1}$). On cooling and reheating we observe the disappearance of the two peaks at 46 and 52 °C and the presence of the peak at 67 °C due to the melting of the red AD_2 complex, as indicated also by the Kofler analysis. This suggests that the AD_2 complex obtained at the solid state by solid–solid interaction can be obtained through the formation of the intermediate AD complex (first endothermic peak) that is not polymeric owing to the presence of excess D.

The broad shape of the peak of the melting of the AD_2 complex indicates that this complex is probably not crystalline. Even for this complex the IR spectra clearly indicate that the ν of the –OH group at 3340 cm^{-1} of the *p*-bromophenol is shifted to 3260 cm^{-1} owing to hydrogen bond formation.

CONCLUSIONS

We think that, even if it is not always possible to obtain useful thermodynamic information from the preparation of complexes in the solid state by solid–solid interaction, nevertheless extending the study to several other systems, some interesting correlations can be obtained. Furthermore, if the purpose is to study the formation of complexes not solvent influenced, useful information can be obtained even when the reaction occurs in a molten component, on condition that the enthalpy of mixing is negligible or can be evaluated.

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