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# FORMATION OF COMPLEXES OF CROWN ETHERS IN THE ABSENCE OF SOLVENT OBSERVED BY DIFFERENTIAL THERMAL ANALYSIS

AILTON DE SOUZA GOMES AND CLARA MARIZE FIREMAND OLIVEIRA
*Núcleo Macromolecular, Universidade Federal do Rio de Janeiro, C.P. 56020–20.000, Rio de Janeiro (Brazil)*
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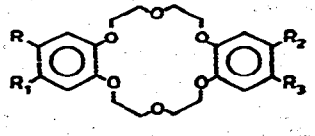
## ABSTRACT

Differential thermal analysis was employed as a new method to observe the formation of complexes of dibenzo-18-crown-6 polyether and macrocyclic nitro derivatives with potassium iodide. DTA thermograms of polyethers, of solid complexes, and mixtures of polyether and potassium iodide were obtained in an atmosphere of dry nitrogen.

## INTRODUCTION

The macrocyclic polyether dibenzo-18-crown-6 (1) can interact with alkali metals to form isolable complexes in appropriate organic solvents Their stability is related to the diameter of the cavity of the polyether ring and the ionic diameter of the cation[1]. The complex between the polyether (1) (cavity diameter 2.6–3.2 Å) and potassium (ionic diameter 2.66 Å) has a 1:1 stoichiometry[2–4].

In this paper we report the results of an investigation of the complex formation, in the absence of solvent, between the polyether (1) and its nitro derivatives (2–4) with potassium iodide, observed by differential thermal (DTA) analyses.




1, $R = R_1 = R_2 = R_3 = H$
2, $R = R_3 = H$, $R_1 = R_2 = NO_2$
3, $R = R_2 = H$, $R_1 = R_3 = NO_2$
4, $R = R_1 = R_2 = R_3 = NO_2$

## EXPERIMENTAL

### *Preparation of the polyethers*

The dibenzo-18-crown-6 (1) was prepared by method X, as previously reported[1], m.p. 162–163°C (lit. 164°C)[1]. Anal. calc. for $C_{20}H_{24}O_6$: C, 66.6; H, 6.6%. Found: C, 66.3; H, 6.6%.

The 20,24-dinitrodibenzo-18-crown-6 (2) and 20,25-dinitrodibenzo-18-crown-6 (3) were also prepared as previously reported[5]. Anal. calc. for $C_{20}H_{22}N_2O_{10}$: C, 53.3; H, 4.9; N, 6.2%. Found for (2), m.p. 245–250°C (lit. 245–251°C)[5]: C, 53.2; H, 4.9; N, 6.3%. Found for (3), m.p. 208–210°C (lit 209–213°C)[5]: C, 53.3; H, 4.9; N, 6.4%.

The 20,21,24,25-tetranitrodibenzo-18-crown-6 (4) was prepared, by the addition of 10 g (27 mmol) of (1) into 80 ml of $HNO_3$ (65%), with magnetic stirring at 4°C during 1 h, followed by addition of 40 ml of $H_2SO_4$ (98%) at 4°C. The reaction mixture was agitated during 10 min at 4°C and the temperature was slowly raised to 60°C. The solution at 25°C was poured into a mixture of ice and water, and the solid product collected and dried yielded 14.3 g (96%). An analytical sample was obtained by recrystallization from DMF (14 g in 250 ml), m.p. 228–229°C. Anal. calc. for $C_{20}H_{20}N_4O_{14}$: C, 44.4; H, 3.7; N, 10.4%. Found: C, 44.7; H, 3.6; N, 10.2%.

*Preparation of the polyether complexes with potassium iodide*

*Potassium iodide complex of dibenzo-18-crown-6 (1).* A solution of 20 ml of methylene chloride, 1.00 g (2.8 mmol) of dibenzo-18-crown-6 (1) and 0.47 g (2.8 mmol) of potassium iodide was shaken vigorously for 40 min. The white crystals were filtered, washed with methylene chloride and dried. The product weighed 0.87 g (57%), m.p. 232–233°C (lit. 232–234°C)[1]. Anal. calc. for $C_{20}H_{24}O_6KI$: C, 45.6; H, 4.5; K, 7.4%. Found: C, 44.2; H, 4.6; K, 7.8%.

*Potassium iodide complexes of dibenzo-18-crown-6 nitro derivatives.* General method. A mixture of polyether, potassium iodide and N,N-dimethylformamide was heated with occasional stirring until the mixture became a clear solution. The solution was cooled to room temperature and benzene was added. The product was filtered, washed with benzene and dried. Anal. calc. for $C_{20}H_{22}N_2O_{10}KI$: C, 38.9; H, 3.6; N, 4.5; K, 6.3%. Found for (2). KI complex, m.p. 285–300°C: C, 39.1; H, 3.7; N, 4.3; K, 6.0%. Found for (3). KI complex, m.p. 245–246°C: C, 37.1; H, 3.7; N, 4.4; K, 5.8%. Anal. calc. for $C_{20}H_{20}N_4O_{14}KI$: C, 34.0; H, 2.8; N, 7.9; K, 5.5%. Found for (4). KI complex decomposition 287–292°C: C, 34.2; H, 2.9; N, 7.9; K, 4.3%.

*Differential thermal analysis*

The DTA curves of polyethers, of crown ether·KI complexes and of mixtures of these macrocyclic polyethers with potassium iodide were obtained in a atmosphere of nitrogen. The heating rate was 10°C $min^{-1}$. A large excess of potassium iodide was used in order to assure a complete complex formation during the heating in the sample holder. A DuPont thermal analyzer Model 990 was employed.

## RESULTS AND DISCUSSION

The polyether complexes were formed in the DTA sample holder in the absence of solvent. A measured amount of the appropriate macrocyclic compound and a large excess of KI were subjected to heating, and the complex formation was detected by

the melting points observed in the thermogram. The complexation is probably taking place during the melting of the crown ether.

In Fig. 1, curve A shows that polyether (I), above its melting point at 160°C, gives a new endothermic peak centered at 330°C, probably caused by distillation of the material, since above this temperature there was no residue in the sample holder. Curve B shows that the KI-macrocyclic (I) complex melts at 235°C and that at 300°C some dissociation and distillation is under way[6]. The endothermic peak at 680°C is the melting point of KI.

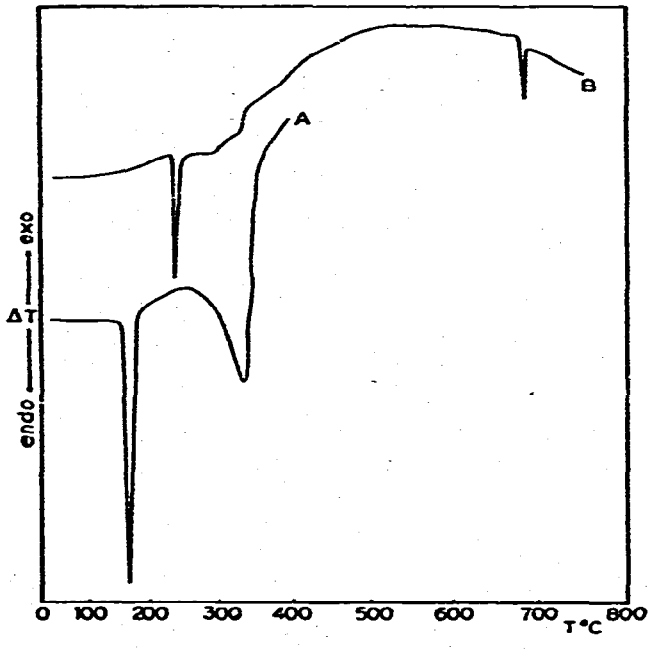



Fig. 1. A = Dibenzo-18-crown-6 (I); B = complex of (I) and potassium iodide.

In Fig. 2, curve A shows the behaviour of the polyether (I) for comparison. Curve B is the DTA curve of the mixture of KI and polyether (I), the heating was interrupted after the melting point of the complex and cooled to room temperature. Curve C is the reheating of the same mixture used for curve B. It clearly shows a complete complex formation. The small endothermic peak at 215°C, not identified, can possibly be assigned to another complex $C_{20}H_{24}O_6 \cdot KI_2$ (m.p. 156–238°C) suggested by Pedersen[1].

Figure 3, curve A shows the thermogram of pure polyether (2). Curve B shows its mixture with a large excess of KI during the heating until just before the beginning of the complex decomposition. The endothermic peak at 280°C is assigned to the melting point of the complex. Curve C was obtained by reheating the cooled sample used for curve B. In this curve there is a small peak at 240°C assigned to the uncomplexed polyether, the endothermic peak at 280°C is the melting point of the complex, which decomposes exothermically at 325°C.

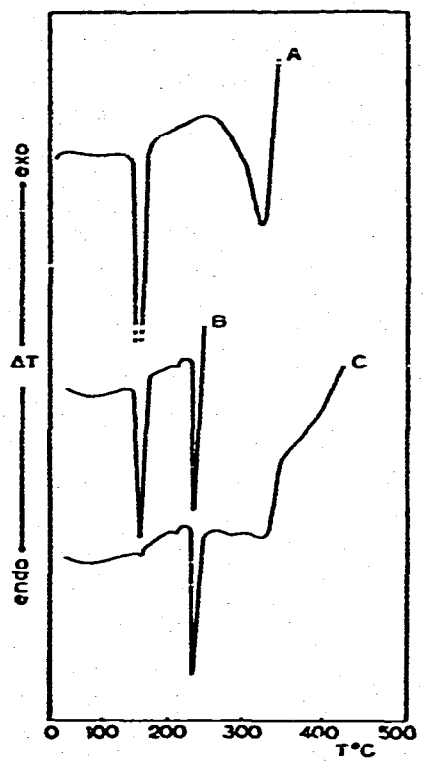



Fig. 2. A = Dibenzo-18-crown-6 (1); B = mixture of KI and (1); C = reheating of B.

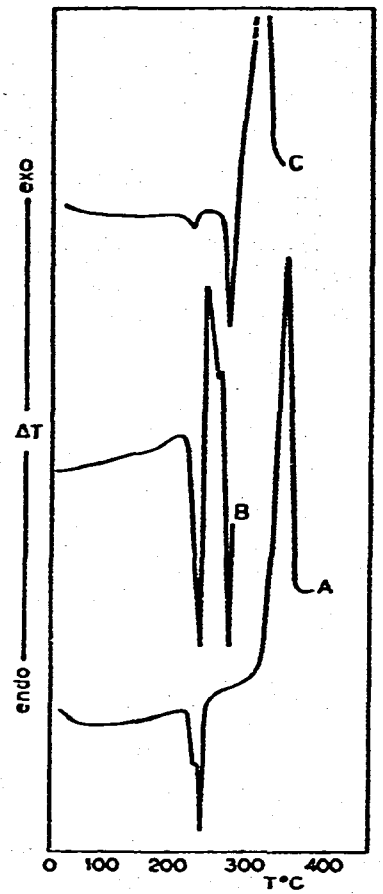
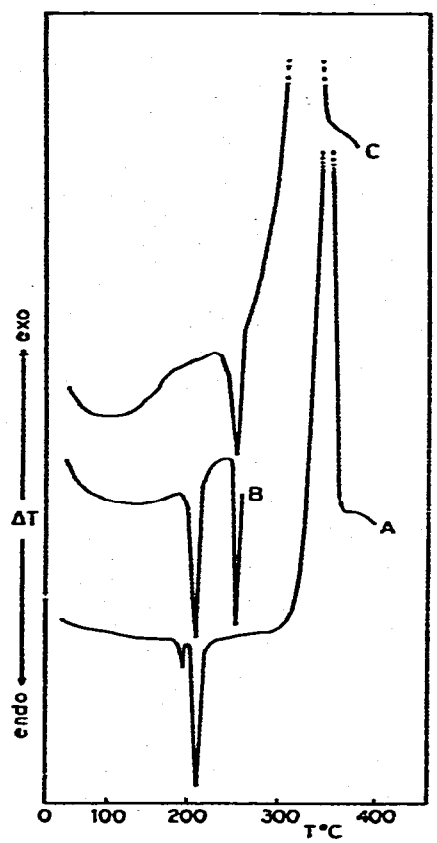



Fig. 3. A = 20,24-Dinitrodibenzo-18-crown-6 (2); B = mixture of KI and (2); C = reheating of B.

Figure 4, curve A shows the thermogram of pure polyether (3). Besides the endothermic peak at 210°C (m.p.) and the exothermic peak at 350°C (decomposition), it shows an endothermic peak at 190°C, not identified, but possibly assigned to a different morphological structure (see combustion analyses), since after heating this polyether to a temperature above 190°C, followed by cooling below 190°C and subsequent heating no peak was observed in this area. Curve B is the thermogram obtained by heating the mixture of KI and polyether (3) just before the temperature of decomposition. Curve C was obtained after cooling the sample from curve B and heating. The temperatures of melting and decomposition clearly indicate the formation of a complex.

The nitro-complex-polyethers (2) and (3) decompose at 350°C while their KI complexes decompose exothermally at 325°C.

Figure 5, curve A shows the thermogram of pure polyether (4), it melts at 228°C and decomposes exothermally at 310°C. Curve B shows the thermogram of a mixture of polyether (4) and an excess of KI. No other endothermic peaks were observed.



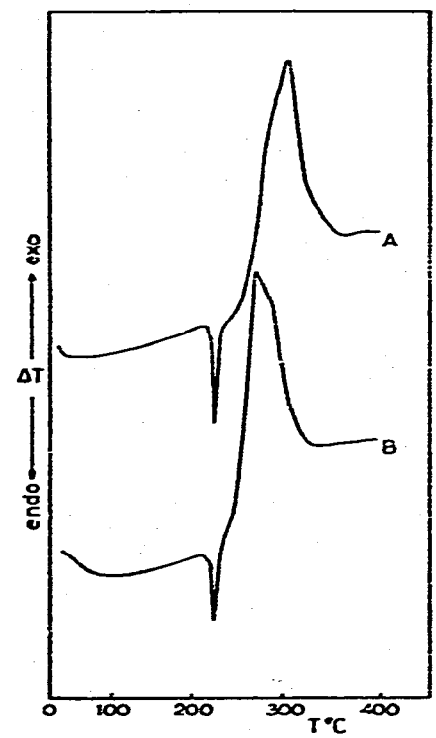




Fig. 4. A = 20,25-Dinitrodibenzo-18-crown-6 (3); B = mixture of KI and (3); C = reheating of B.

Fig. 5. A = 20,21,24,25-Tetranitrodibenzo-18-crown-6 (4); B = mixture of KI and (4).

However, decomposition takes place at 296°C exothermally, which clearly indicates that complexation took place.

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