

Based on the values presented in Table 1 we can state that *iso*-propyl isocyanate has a lower boiling point than the melting point of *o*-nitrophenyl carbamate from which it can be obtained, while benzyl isocyanate's boiling point is very close to the melting point of *N*-benzyl-*o*-nitrophenyl carbamate. The other two isocyanates have higher boiling points as compared to the melting points of the corresponding *o*-nitrophenyl carbamates.

The thermal analysis dealt with differential scanning calorimetry (DSC), which gives the temperatures at which physical or chemical transformations, endo-and exothermal, occur, and thermogravimetry (TG) techniques, which can determine mass loss as a function of temperature. The heating rate used for all these studies was 5°C/min.

From the DSC thermograms (Figures 1a-4a) it can be seen, as general characteristic, that only endothermal changes take place here and none of the analyzed samples decomposed before the melting point.

The TG plots (Figures 1b-4b) show that mass loss (carbamate decomposition), occurred in only one step, the vaporization of the isocyanate and *o*-nitrophenol taking place almost in the same time.

The DSC thermogram for *N*-*iso*-propyl-*o*-nitrophenyl carbamate (1) (Figure 1a) shows an endothermal peak at 81.9°C, corresponding to its melting point, and the decomposition starts at about 120°C, with the decomposition peak at 198°C. The TG curve (Figure 1b) shows that the mass loss starts at about 110°C and ends at 180°C.

N-*sec*-butyl-*o*-nitrophenyl carbamate (2) starts melting at the lowest temperature, 59.8°C, but the DSC thermogram (Figure 2a) indicates that the decomposition only begins around 150°C, with a minimum at 214°C (the value at which *o*-nitrophenol boils), even though the boiling point of the isocyanate is 101-102°C. The TG plot (Figure 2b) shows that the mass loss occurs again in only one step, but it starts at approximately 100°C and ends at 200°C.

In the *N*-cyclohexyl-*o*-nitrophenyl carbamate (3) case, we notice that the DSC thermogram (Figure 3a) displays two endotherm peaks: one that corresponds to the melting point (144.7°C) and a wider one at 218°C, from the decomposition process. According to the thermogram, the decomposition begins around 155-160°C. The TG plot indicates that mass loss starts at a temperature below 140°C and ends around 200°C.

N-benzyl-*o*-nitrophenyl carbamate (4) has a melting point of about the same temperature (83.6°C) as the boiling point of the isocyanate (84-87°C) obtained from the decomposition. Still, the DSC thermogram (Figure 4) shows that the decomposition only starts around 120°C, and the wide peak whose minimum occurs at 207°C has a 'shoulder' at 159°C. This DSC thermogram best exemplifies the decomposition process, starting with the isocyanate elimination and followed by the *o*-nitrophenol elimination. In the TG plot (Figure 4b) we can observe that mass loss starts at about 110°C and ends at roughly 200°C.

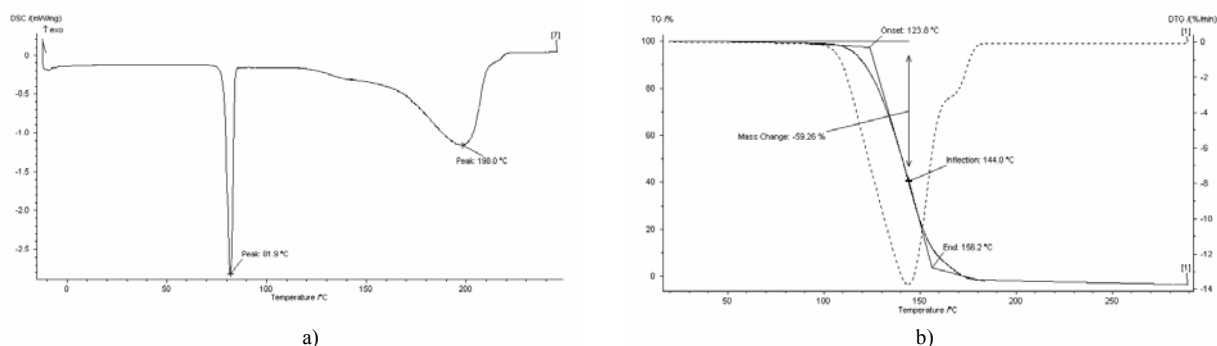


Figure 1. DSC (a) and TG (b) curves for the thermal decomposition of *N*-*iso*-propyl-*o*-nitrophenyl carbamate at 5°C/min

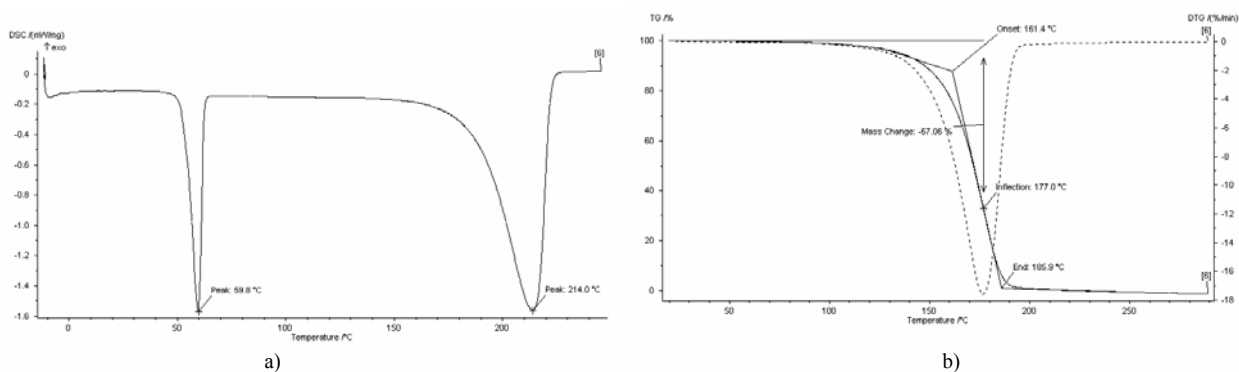
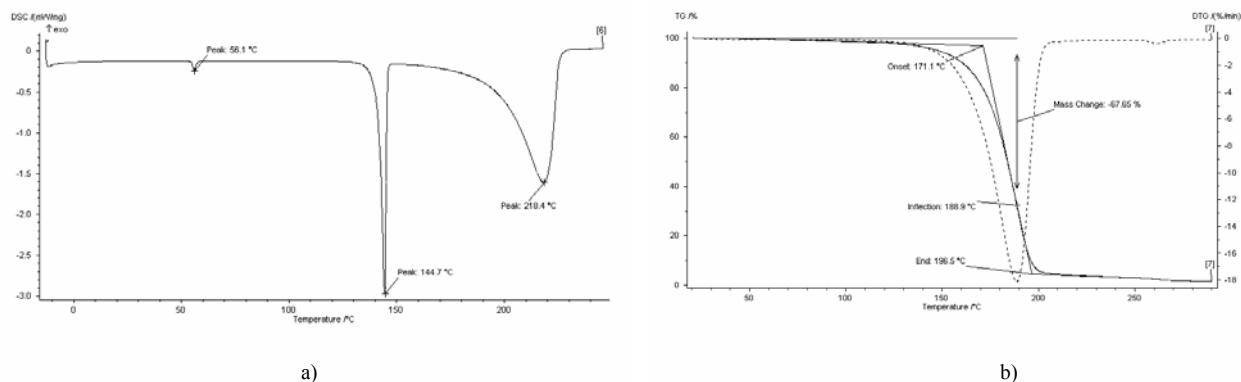
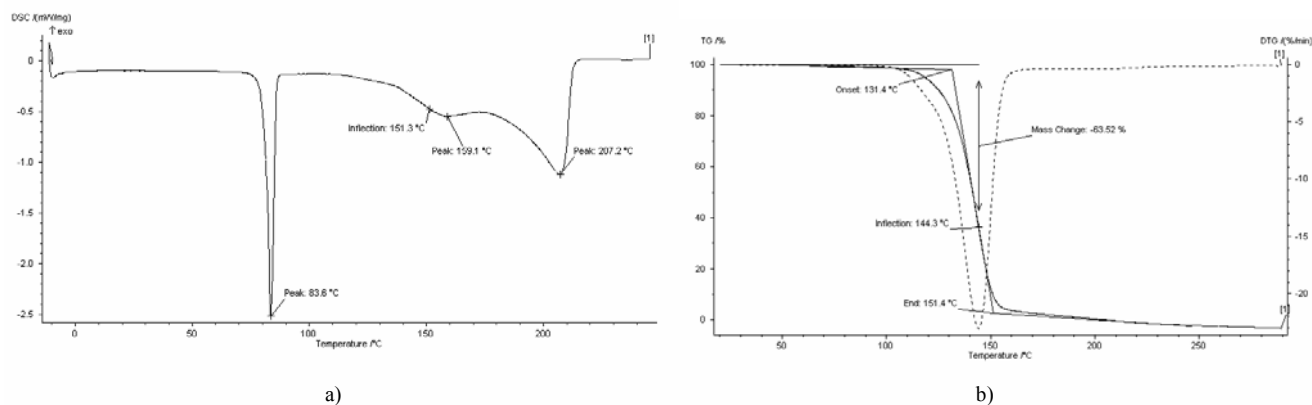


Figure 2. DSC (a) and TG (b) curves for the thermal decomposition of *N*-*sec*-butyl-*o*-nitrophenyl carbamate at 5°C/min

Figure 3. DSC (a) and TG (b) curves for the thermal decomposition of *N*-cyclohexyl-*o*-nitrophenyl carbamate at 5°C/minFigure 4. DSC (a) and TG (b) curves for the thermal decomposition of *N*-benzyl-*o*-nitrophenyl carbamate at 5°C/min

4. Conclusions

Based on all the above stated, we can conclude that these carbamates are stable at temperatures that are lower than their melting point. Therefore when they get to the decomposition temperature and split into isocyanate and *o*-nitrophenol, they leave the system almost in the same time, regardless of the difference in their melting point.

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