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Thermal decomposition and stability of quinoline compounds using thermogravimetry and differential scanning calorimetry

Elena Lizarraga*, Camino Zabaleta, Juan A. Palop

Department of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Navarra, Irunlarrea 1, 31008 Pamplona, Spain

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Abstract

Thermal analysis, with DSC and TGA of fusion and decomposition processes of some quinoline compounds were carried out to determine their stability. The quinoline compounds are classified by the R_6 sustituent: NO_2, $NHCOCH_3$, H or OCH_3 and they have a variable substitution in position 1. Certain factors in the substitution (length of chain, chain branching and unsaturation) are not especially relevant to the physical stability. The compounds are very polar and the dipole–dipole forces give stability to the crystal. An increase in the physical stability is also observed with aromaticity and when halogens are present. An increase in the chemical stability, from the acetylamine group to the nitro group, is observed.

Keywords: Degradation process; Thermal analysis; Thermal decomposition; Quinolines

1. Introduction

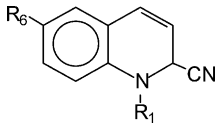
The application of thermal methods to organic compounds of potential pharmacological action can be of great use for determining their physical and chemical stability [1–5].

Predicting stability or instability at a very early stage of product development, such as immediately after the initial synthesis process, provides valuable information.

In the description of a degradation reaction of an organic compound, most compounds melt, decompose, sublimate or volatilize [6]. The decomposition can be accompanied by a superficial fusion or by the formation of liquid products in which the reagent is soluble. The reaction can take place simultaneously in the homogeneous phase as well as in the heterogeneous phase. Nevertheless, there is a tendency for decomposition to be more rapid in the homogeneous condition than in the heterogeneous condition.

2. Material

Asymmetric compounds of variable disubstitution have been selected; these structures are referable to a general formula that consists of an invariable matrix of quinoline structure on which a variable substitution is carried out in positions 1 and 6, with substituents of diverse nature. Compounds that carry both aromatic and aliphatic parts, of diverse polarity and geometry, and are distributed heterogeneously throughout the molecule, are obtained.



In the following series, the compounds are classified in terms of the R_6 substituent: series A: $R_6 = NO_2$; series B: $R_6 = NHCOCH_3$; series C: $R_6 = H$ and series D: $R_6 = OCH_3$.

3. Methodology

The calorimetric studies are carried out with a Perkin-Elmer, DSC-7, and thermogravimetric studies with a Perkin-Elmer, TGA-7.

* Corresponding author. Tel.: +34 948 425653; fax: +34 948 425652.
E-mail address: elizarraga@unav.es (E. Lizarraga).

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Calorimetric analyses are performed at 10 °C/min in aluminium capsules for volatiles of 10 μL, to find the T_{onset}, T_{max} and the enthalpy of fusion, ΔH_f. In some cases, the T_{onset}, T_{max} and ΔH of the exothermal degradation are calculated. The analyses are performed in high-pressure capsules, at 10 °C/min and under nitrogen atmosphere.

Thermogravimetric analyses are carried out at 10 °C/min (under air atmosphere with a gas flow of 40 mL/min). The $T_{initial}$, T_{onset} and T_{max}, as well as any associated weight loss, are calculated. Likewise, if the degradation process develops in several stages, the temperature at which the first stage finishes is calculated; this temperature is called T_{1-2}, and the associated weight loss is referred to as w_∞.

4. Results and discussion

Series A ($R_6 = NO_2$): the presence of halogens causes an increase in temperature and enthalpy of fusion. In addition, the chain length of the substituent in position 1 of the quinoline matrix influences compound physical stability. An increase in the chain length provokes decreases in the temperature, enthalpy of fusion, and physical stability of the compound. Unsaturation and the chain branching seem to be determinant factors (Table 1).

Series B ($R_6 = NHCOCH_3$): a decrease in the temperature and enthalpy of fusion occurs when the chain is lengthened. With regard to chain branching, the temperature and enthalpy of fusion values increase towards the linear compound (Table 2).

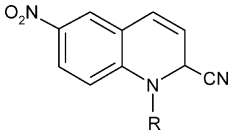
Series C ($R_6 = H$): the length of the chain and/or the branching result in an increase in the stability. Once again, the presence of halogens gives rise to products with high temperatures and enthalpies of fusion, meaning products that are physically more stable (Table 3).

Series D ($R_6 = OCH_3$): the influence exerted by the length of the chain is observed once more. When this length increases, the temperature and enthalpy of fusion values decrease. In addition, when branching of the chain in position 1 increases, so does the stability. The physical stability increases with aromaticity and presence of halogens (Table 4).

4.1. Conclusions regarding the physical stability

The previously mentioned factors (length of chain, branching and unsaturation) are not especially relevant. When the principal molecule of this group is structurally analyzed, it is observed that the compounds present an amide or carbamate group in position 1, which give the compounds

Table 1
Fusion and degradation processes of nitro-substituent quinoline compounds



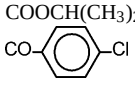
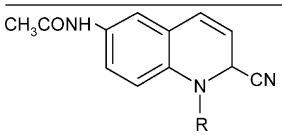
	Series A		
	Fusion process (DSC)		Degradation process (TGA)
R	T_{onset} (°C)	ΔH_f (J/g)	T_{onset} (°C)
$COOCH(CH_3)_2$	128.8	96.6	236.1
	157.3	75.4	218.4
$COOCH_2CH_2CH_2CH_3$	85.9	83.5	244.0
$COOCH_2CH_2CH_3$	99.0	87.0	237.7
$COOCH_2CH_2Br$	146.0	56.2	225.8
$COOCH_2CH_3$	118.0	99.2	227.0
$COOCH_2CH{=}CH_2$	110.5	94.2	220.1
$COOC(CH_3){=}CH_2$	116.2	92.1	231.6
$COCH_2CH_2Cl$	145.7	55.8	236.2
$COOCH_2CH(CH_3)_2$	115.6	93.8	251.9

Table 2
Fusion and degradation processes of acetylamide-substituent quinoline compounds



	Series B		
	Fusion process (DSC)		Degradation process (TGA)
R	T_{onset} (°C)	ΔH_f (J/g)	T_{onset} (°C)
$COOCH_2CH_2CH_3$	–	–	168.4
$COOCH_2CH(CH_3)_2$	131.4	63.3	173.1
$COCH(CH_3)_2$	104.2	42.3	178.7
$COOCH_2CH_2CH_2CH_3$	162.9	116.3	182.1
$COOCH_2CH_3$	168.0	122.8	160.6