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DECOMPOSITION STUDIES OF OXETANES DERIVED FROM CARBONYL COMPOUNDS AND FIVE-MEMBERED HETEROCYCLICS BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The temperature, heat and entropy of fusion and the temperature of decomposition of oxetanes derived from photochemical reaction between the five-membered heterocyclics, containing O, N and S, respectively, as the hetero-atom and several excited carbonyl compounds have been measured. These characteristics are intended to serve as supplemental data for the identification of this type of compound. Furthermore, this investigation establishes the general pattern in the thermal behavior of this family of compounds containing as a common feature a four-membered ring with an oxygen atom.

INTRODUCTION

It has been possible to prepare in this laboratory oxetanes from furan[1], pyrrole[2] and thiophene[3] derivatives in photochemical reactions with carbonyl compounds such as benzophenone, 1-naphthaldehyde[4] and 2-, 3-, and 4-benzoylpyridines[4] according to the general reaction (Fig. 1). These compounds have been

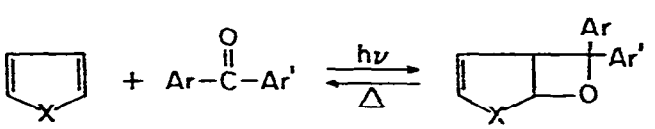


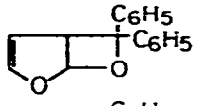
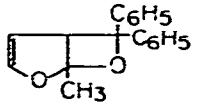
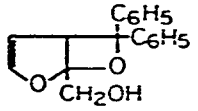
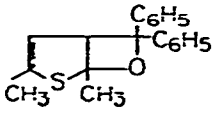
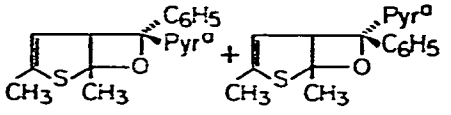
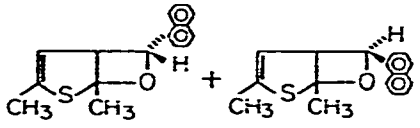
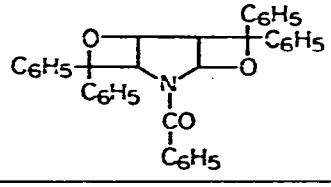
Fig. 1. General reaction for the formation and decomposition of the oxetanes. X = O, S, N–COPh.

found to be generally thermally stable even though some of them slowly decompose on standing at room temperature. From a practical point of view, it has been shown that some oxetanes may be useful as fungicides[5]. On the other hand, they are chemically interesting substances, due to the fact that they contain a strained four-membered ring with an oxygen atom. Therefore, it was of interest to investigate their thermal properties by means of differential scanning calorimetry. That is to say, it appeared interesting to find out if the physical and chemical transitions undergone by these compounds under heating present a common pattern.

The series of compounds studied may be illustrated in Table 1.

TABLE 1

OXETANES STUDIED BY DSC

Ketone	Heterocyclic	Oxetane	
Benzophenone	Furan		*I*
Benzophenone	2-Methylfuran		*II*
Benzophenone	2-Furfuryl-alcohol		*III*
Benzophenone	2,5-Dimethyl-thiophene		*IV*
2-,3-, and 4-Benzoylpyridine	2,5-Dimethyl-thiophene		*V* *VI* *VII*
1-Naphthaldehyde	2,5-Dimethyl-thiophene		*VIII*
Benzophenone	1-Benzoyl-pyrrole		*IX*

[a] Pyr = 2-pyridyl (in V), 3-pyridyl (in VI), 4-pyridyl (in VII)

EXPERIMENTAL

Synthesis of oxetanes

The general procedure for the preparation of the oxetanes was to dissolve 1 g of the carbonyl compound in 75 ml of the heterocyclic compound. The reaction mixture was irradiated with a Hanovia 450 w. mercury arc. in a quartz apparatus with a filter pyrex sleeve at −10°C. Nitrogen was bubbled through the solution before and during irradiation. After 8 h exposure to UV light the irradiation was stopped and the solvent distilled under vacuum. In most cases the residue readily crystallized. In case it did not solidify treatment with methanol induced crystallization. The

compounds were identified and their purity verified by their mass and nuclear magnetic resonance spectra. Since N-benzoylpyrrole is a thick oil, the photolysis of benzophenone with this compound was carried out using benzene as the solvent.

Scanning calorimetry

Differential scanning calorimetry (DSC) was carried out in a DuPont DSC module used in conjunction with the Analyser Model 990 console, at a heating rate of 5°C min^{-1} in the range of 25–500°C. Non-hermetic pans were used. The DSC was calibrated by running melting curves with metallic indium. The oxetanes were recrystallized from suitable solvent systems (generally acetone–methanol) and dried under vacuum. Samples ranging from 5.0 to 10.0 mg, with an accuracy of within ±0.1 mg, were weighed. Furthermore, samples of the parent carbonyl compound were also prepared and heated under the same conditions as those used for the oxetanes (Fig. 2). Each sample was heated to the decomposition point and the products obtained were analyzed by means of a Hitachi–Perkin-Elmer RMV-6H mass spectrometer.

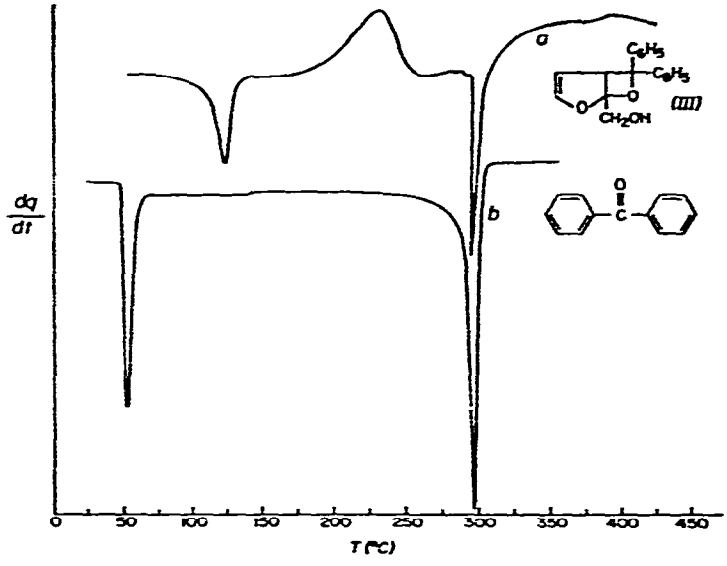


Fig. 2. Representative differential scanning calorimetry curves for an oxetane and parent carbonyl compound.

The reversibility of the melting point was verified by taking the melting point twice in succession for the same sample. That is to say, after the first determination the temperature was allowed to go up 5°C higher, then the sample was cooled and the melting point determined once more. If the value corresponding to the area of the fusion peak after the second determination is smaller than that after the first determination, it is inferred that the compound melts with decomposition. Alternatively, the compounds which melt with decomposition were also investigated varying the

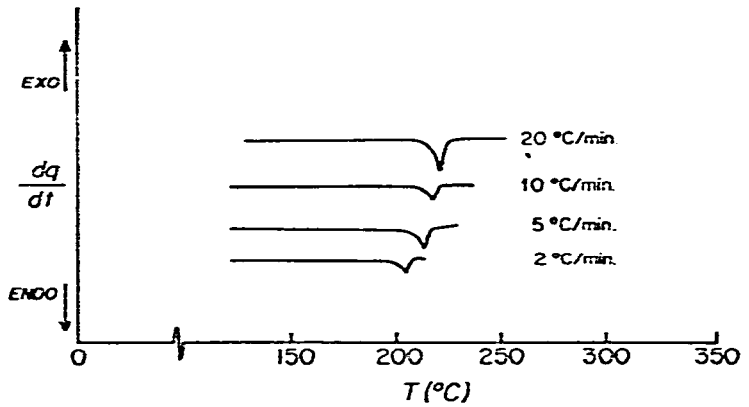


Fig. 3. Displacement of the vertex of the melting peak on varying the rate of heating of compound IX.

rate of heating[6] (compounds VIII and IX). Thus, after the calibration of the instrument with indium (m.p. 156.6°C), samples of these compounds (2–3 mg) were heated at heating rates of 20, 10, 5 and 2°C min^{-1}, respectively. For compound IX, for example, the vertex of the melting peak was shifted from 219, to 216, 213 and 204°C, respectively, (Fig. 3). In the thermogram of compounds, which melt with decomposition (Fig. 4), the fusion and the decomposition bands are observed so close to each other that it is rather difficult to determine values for either ΔH_f or ΔH_d. When the photoproducts (V, VI and VII) derive from compounds where the carbonyl group is asymetrically substituted, such as the benzoylpyridines, the oxetanes consist of a mixture of two geometrical isomers which are extremely difficult to separate; in such cases the enthalpy of fusion and decomposition were not determined. For the calculation of ΔH_f and ΔH_d, five determinations were carried out for each compound. The area under the bands was determined with a Keufel and Esser

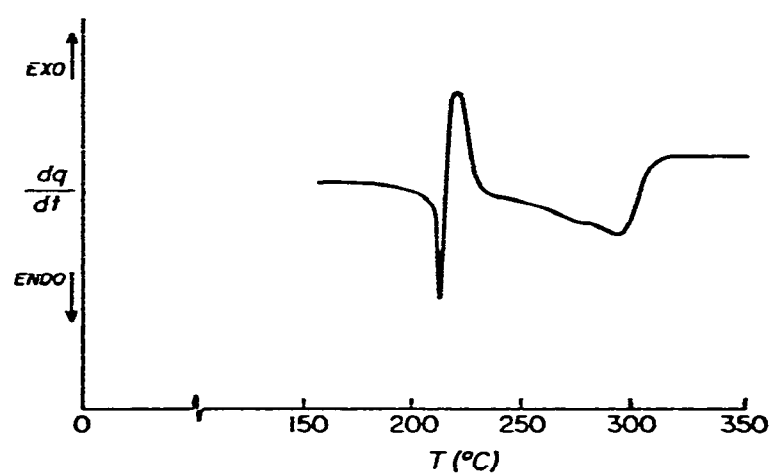


Fig. 4. Differential scanning calorimetry curve for a compound (IX) that melts with decomposition.

planimeter. In order to draw the baseline which determines the area for each transition the criterion of Guttman[7] was used. If the mean deviation in the determination of the area with the planimeter is greater than 3%, the area was then determined by weight of the peak cut out from the graph paper. Values of ΔH were calculated according to the method illustrated in the Dupont Manual for the Model 990 thermal analyser. The five determinations for each compound were averaged. Values whose deviation (x_i) from the average value is $x_i \geqq 2{,}5d$[9], (where d is the average deviation) were discarded. From the acceptable values the standard deviation[10], S was calculated. The results are summarized in Table 2. ΔS_f was calculated by taking the ratio ΔH_f/m.p.

TABLE 2

THERMAL PROPERTIES OF THE OXETANES

Oxetane	m.p. °C	Td °C	ΔHf kcal/mole	ΔSf cal/mole K	ΔHd kcal/mole
I	103	227	2.70(±0.01)[a]	7.18(±0.08)	7.29(±0.43)
II	145	205	2.74(±0.08)	6.56(±0.24)	1.26(±0.08)
III	123	230	2.21(±0.29)	5.58(±0.79)	6.16(±0.54)
IV	160	245	4.71(±0.48)	11(±1)	3.88(±0.04)
V	113	170	b	———	———
VI	133	235	b	———	———
VII	190	235	b	———	———
VIII	115	145	c	———	———
IX	213	221	c	———	———

a Values in parenthesis represent standard deviation

b Mixture of geometrical isomers

c Melt with decomposition

Td = decomposition point

RESULTS AND DISCUSSION

In general all the compounds studied present a common pattern in the DSC curves. Namely, it consists of three peaks in the following order: endotherm, exotherm, endotherm, as illustrated in Fig. 2a (a similar behavior could be expected for all the photocyclo-addition and Diels–Alder compounds). The first peak indicates the melting of sample, the second the decomposition of the oxetane and the third corresponds to the boiling point of the carbonyl compound, as illustrated in Fig. 2b. The evaporation of the carbonyl compound was verified by running a sample of the corresponding parent carbonyl compound and observing the coincidence of the last peak in the DSC curve for oxetane with the second peak of the DSC curve for the carbonyl compound. The oxetanes decompose to their starting materials, namely,

heterocyclic and carbonyl compound as demonstrated by the mass spectrometry of the products obtained at temperature T_d (see Table 2). These products were condensed and injected in the mass spectrometer. It is interesting to note that the oxetanes undergo the same type of decomposition under the conditions of mass spectrometry. In other words, they undergo a Retro-Diels–Alder type of fragmentation. Compounds V, VI and VII are not single compounds as is said above; these have been useful only to illustrate the general pattern of the DSC curve. However, under the circumstances no values for ΔH_f and ΔH_d have been calculated for them. Compounds VIII and IX melt with decomposition and their curves such as in Fig. 3 do not allow a good calculation of ΔH_f and ΔH_d.

The values of ΔS_f for the oxetanes agree qualitatively with the correlations between molecular structure and entropy of fusion commented by Bondi[8]. They found that the entropy of fusion rises rapidly as the molecular weight increases. Nevertheless, this phenomenon occurs very markedly for long open-chain compounds while for rigid molecules this increase is very slow and it reaches a limiting value that does not exceed 13 to 15 cal K^{-1} mol^{-1}. Since these oxetanes are rigid molecules it is reasonable to expect ΔS_f values lower than 13–15 cal K^{-1} mol^{-1}, as indeed, it occurs, in spite of the fact that they have 19 to 23 carbon atoms.

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