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Note

Thermal and mass spectral fragmentation studies of some acid phthalic esters

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Abstract

1-Phenylethyl hydrogen phthalate (*I*) and 1-(p-*t*-butyl)-phenylethyl hydrogen phthalate (*II*) were subjected to thermogravimetric analysis and mass spectral fragmentation studies. During thermolysis these esters gave phthalic anhydride and the respective carbinols. The mass spectral fragmentation pattern appears to support the thermal fragmentation pattern. The results are discussed in the light of similar earlier studies on some acid terepthalic esters.

EXPERIMENTAL

The acid phthalic esters *I* and *II* were prepared as high purity products using known methods [1]. The TG curves were recorded using a Stanton recording thermobalance (model TR-1). Accurately weighed quantities of the samples (about 40 mg) were used in the TG analysis in static air with a heating rate of 4°C min^{-1}. The mass spectrum was recorded on a Varian MAT CH7 mass spectrometer (filament current and potential being 100 A and 70 eV, respectively).

RESULTS AND DISCUSSION

The TG curves, drawn as mass against temperature, of *I* and *II* are given in Fig. 1. In both cases, the mass loss appears to be a two-stage process with some overlapping. It may be recalled at this stage that well defined and non-overlapping TG traces were obtained in similar studies with acid terephthalic esters of 1-phenylethyl alcohol and its *p*-ethyl derivative and that in those cases the first stage of the thermal decomposition agreed quantitatively with the removal of the styrenes derivable from the alcohol parts of the esters [2]. The other product in the earlier investigation was terephthalic acid. In the present case with acid phthalic esters, however, the products were phthalic anhydride and the respective carbinol. Unlike in the case of the acid terephthalic esters, styrenes were not found to be a pyrolysis product. The mass loss during the first stage of thermolysis of *I* and *II* is

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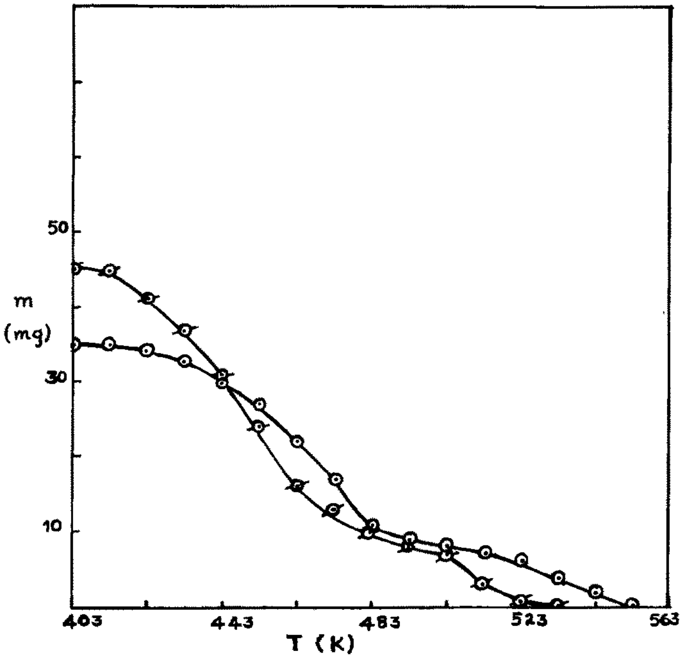


Fig. 1. Mass versus temperature for the thermal decomposition of *I* (⊙) and *II* (-⊙-).

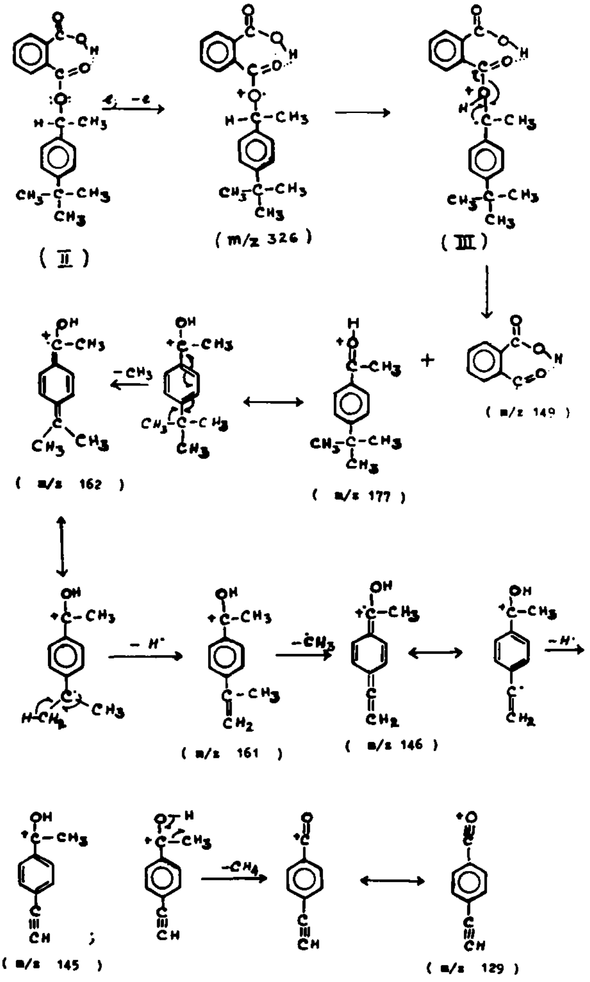
about 65% by weight. Theoretically, loss of carbinol from *I* amounts to 45% by weight and that from *II* is 55%. Prior to thermal decomposition, the acid phthalates melted and, unlike in the case of the acid terepthalates, the molten mass did not solidify at the onset of decomposition. In separate experiments, the molten acid phthalic ester was found to contain phthalic anhydride when suddenly cooled and analysed. The larger percentage of weight loss in the first stage can therefore arise from volatalisation of the anhydride at the temperatures at which the decomposition occurs rapidly; hence, the overlapping of the stages.

The mass spectral data of *II* are presented in Table 1. In earlier investigations with the acid terephthalic esters it was found that the thermal decomposition pattern and the mass spectral fragmentation patterns were complementary [2,3]. In the present study, the same trend was also observed. The molecular ion peak of the substrate *II* was found at m/z 326. The molecular ion having m/z 149 was found with a relative abundance of 20%. The formation of this ion is characteristic of phthalic acid esters [4]. The base peak was found at m/z 177 and it appears to arise from the alcohol moiety of the ester. It is significant that the phthalic acid ion peak (m/z 166) is absent. Similarly the absence of the ion of m/z 160 indicates absence of formation of the styrene molecular ion obtainable from the alcohol moiety of the ester, *II*. Styrene and terephthalic acid molecular ions have been detected in good percentage abundances in similar studies with the acid terephthalic esters [3].

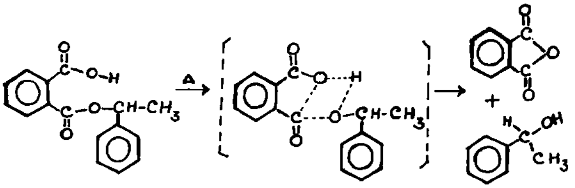
TABLE 1

Mass spectral data of 1-(*p*-*t*-butyl) phenylethyl hydrogen phthalate

m/z	Relative abundance (%)	*m/z*	Relative abundance (%)
57	34	131	12
65	16	145	38
77	8	149	20
91	14	161	22
93	8	177	100
105	12	178	32
121	23	179	6
		326	6



Scheme 1.



Scheme 2.

In the case of compounds *I* and *II*, one would normally expect an electron on either of the two carbonyl atoms to be most readily lost during electron impact. However, intramolecular hydrogen bonding apparently seems to increase the threshold energy needed for removal of one of these electrons. Therefore, it seems more likely that the alkyl oxygen loses an electron during electron impact; the most populous ion seems to be that represented by structure *III* given in Scheme 1. The above scheme also accounts for the low relative abundance of the signal at *m/z* 149 and the absence of any signal at *m/z* 148. The signals at *m/z* 121, 105 and 77 are likely to arise from the ion with *m/z* 149.

Thus, it can be seen that thermal decomposition of acid phthalic esters gave phthalic anhydride and the carbinol, while acid terephthalic esters gave terephthalic acid and styrene. In either case the mass spectral data are found to be complementary to the thermal data. During the thermal decomposition of the acid phthalic esters, it is quite likely that decomposition takes place through formation of a four-centre transition state (as shown in Scheme 2) which resembles the four-centre electrophilic–nucleophilic process proposed by Bender et al. for the hydrolysis of phthalamic acid [5].

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