Pyrolysis of cyclo-aromatic diesters

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Abstract Studies on the pyrolysis of cyclo-aromatic diesters derivatives of 3-phenylprop-2-en-1-ol are presented. The diesters are obtained during catalyzed esterification process of a stoichiometric ratio of 3-phenylprop-2-en-1-ol with suitable cycloaliphatic or aromatic acid anhydride in the solvent-free medium. As an acid anhydrides cyclohexane-1,2-dicarboxylic anhydride, *cis*-4-cyclohexene-1,2-dicarboxylic anhydride, bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride, and phthalic anhydride were applied. The thermal properties of obtained compounds under inert atmosphere were tested by means of differential scanning calorimetry and thermogravimetry coupled with FTIR analysis. The pyrolysis products were determined and the probable mechanism of their decomposition was proposed.

Keywords Esterification · 3-Phenylprop-2-en-1-ol · Pyrolysis · DSC · TG/FTIR

Introduction

Thermogravimetric analysis is one of the most useful techniques of thermal analysis. It is commonly applied to characterize the thermal behavior of various compounds. This technique measures the mass loss as a function of temperature or time. It allows understanding the thermal degradation pathways and degradation kinetics of polymers, organic or inorganic compounds [1–7]. Also, it

makes it possible to study the evaporation process, product and component stability, and changes in component properties during heating in inert or oxidative atmospheres, which is a necessary knowledge in order to find the practical applications of many compounds. In addition, the TG coupled to FTIR or QMS allows identifying the compounds which are released during decomposition or degradation process of studied materials. It can be useful in characterization of the decomposition and thermal degradation mechanism of polymers, copolymers, inorganic and organic compounds [8–13], oxidation of materials [14–18], and in estimation of possible air pollution during manufacturing the materials in high temperatures.

In our previous papers, we have used the techniques of thermal analysis coupled to FTIR or/and QMS to study the degradation mechanism under pyrolysis or oxidation conditions of aliphatic, linear chain diesters [19, 20]. Such compounds can be successfully applied as low volatile compounds to many practical applications, especially as aroma compounds which are widely used in cosmetic, perfumery, and food industries as a flavor and fragrance components [19–23].

According to literature survey, among the aromatic esters the most valuable and important fragrance and flavor substances are the monoesters which are obtained during esterification process of aromatic alcohols e.g., benzyl alcohol, 2-phenylethyl alcohol, 1-phenylethyl alcohol, 3-phenylpropanol, 1-phenyl-2-methyl-2-propanol, or cinnamic alcohol with the suitable aliphatic monoacid or acid anhydride [24–27]. However, rare information is available on the preparation and thermal characterization of cyclo-aromatic diesters derivatives of 3-phenylprop-2-en-1-ol. The main objective of the present paper is to study the thermal stability and the degradation mechanism of aromatic and cyclo-aromatic diesters derivatives of naturally

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occurring alcohol: 3-phenylprop-2-en-1-ol. The information regarding the thermal stability and degradation mechanism of those compounds can help to evaluate their possible practical applications. Due to the pleasant, balsamic odor they can find their place as flavor and fragrance ingredients added to many products, e.g., for polymers, plastics, and their commercial products particularly manufactured at high-temperature processing.

Experimental

Materials

3-Phenylprop-2-en-1-ol (98 %) was from Fluka. Phthalic anhydride (98 %), cyclohexane-1,2-dicarboxylic anhydride (98 %), 4-cyclohexene-1,2-dicarboxylic anhydride (98 %) and bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride (97 %) were delivered by Merck. Butylstannous acid was obtained from Arkema Inc., USA. The reagents were used as received.

Synthesis of esters

The unsaturated, cyclo-aromatic diesters were obtained during esterification reaction of 3-phenylprop-2-en-1-ol with cycloaliphatic acid anhydrides in the free-solvent medium. The concentration of reagents was constant. The concentration of 3-phenylprop-2-en-1-ol was 2.04 mol dm^{-3} , the concentration of an acid anhydride was 1.02 mol dm^{-3} , respectively. The reaction was carried out in the presence of butylstannous acid as a catalyst (0.1 mass%). The reaction temperature was continuously increased from 135 to 155 °C as the progress of the reaction increased. The progress of the esterification process was measured by the determination of the residual acid content. Acid number (mgKOH/g) was evaluated by titration of the sample against potassium hydroxide using phenolphthalein as an indicator and acetone as a solvent. The drop of an acid number below value 5 mgKOH/g was the indication of the process completion. The scheme of the synthesis of cyclo-aromatic diesters is presented in Fig. 1. Their structure was confirmed based on spectroscopic methods (NMR and ATR-FTIR analyses).

Characterization

^1H -NMR spectra were obtained using an NMR Bruker-Avance 300 MSL (Germany) spectrometer at 300 MHz. The CDCl_3 was used as the solvent. The TMS was applied as an internal standard. ^1H NMR chemical shifts in parts per million (ppm) were reported downfield from 0.00 ppm with the use of TMS.

^{13}C NMR spectra were gathered on a Bruker 300MSL instrument (Germany). Chemical shifts were referred to chloroform serving as an internal standard.

ATR-FTIR spectra were recorded on a Tensor 27 Bruker (Germany) spectrometer equipped with diamond crystal. The spectra were recorded in the spectral range of $600\text{--}4,000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} and 16 scans.

Elemental analysis was made using a Perkin Elmer CHN 2400 analyser (USA)

Viscosity at 25 °C was estimated using rotating spindle rheometer, Brookfield, model DV-III (Germany).

Density at 23 °C was measured with the use of a glass pycnometer with capillary fuse Gay/Lussac (25 mL).

Refractive index was determined by the use of refractometer Carl Zeis Jena at 23 °C.

Thermal studies

Differential scanning calorimetry analysis was performed with the use of a DSC 204 calorimeter, Netzsch (Germany). All DSC measurements were carried out in Al pans with pierced lid. As a reference empty Al crucible was applied. The mass of the sample was about 10 mg. The dynamic scans were performed at a heating rate of 10 °C min^{-1} from 20 to 500 °C under argon atmosphere (20 mL min^{-1}).

Thermal analysis was carried out on a STA 449 Jupiter F1, Netzsch (Germany). All measurements were made in Al_2O_3 crucibles. As a reference empty Al_2O_3 crucible was applied. Dynamic scans were performed at a heating rate of 10 °C min^{-1} under helium atmosphere (40 mL min^{-1}) from 40 to 700 °C. The sample weight was about 10 mg.

The gas composition evolved during heating process was analyzed by FT IR spectrometer Bruker TGA 585

Fig. 1 The scheme of the esterification process

(Germany) coupling on-line to STA instrument. The FTIR spectrometer with IR cell maintained at 200 °C was connected on-line to STA instrument by a Teflon transfer line with diameter of 2 mm heated to 200 °C. The FTIR spectra were recorded in the spectral range of 600–4,000 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans per spectrum.

Results and discussion

Characterization

The structures of the four new compounds are shown in Fig. 2. As it is visible the esters differ in their structure. They contain various acid units such as aromatic (1), cyclohexane (2), cyclohexene (3), or bicyclo (4) rings. Chemical structures of prepared esters were confirmed by elemental analysis, Table 1 and spectroscopic methods. The ATR-FTIR

Fig. 2 The structure of the unsaturated (cyclo)-aromatic diesters

Table 1 Elemental analysis of newly obtained compounds

Compound	Formula	$M/\text{g mol}^{-1}$	$w, \text{calc.}/\% \quad w, \text{found}/\%$	
			C	H
1	$\text{C}_{26}\text{H}_{22}\text{O}_4$	398.46	78.37 78.33	5.56 5.50
2	$\text{C}_{26}\text{H}_{28}\text{O}_4$	404.51	77.20 77.16	6.98 6.95
3	$\text{C}_{26}\text{H}_{26}\text{O}_4$	402.49	77.59 77.52	6.51 6.45
4	$\text{C}_{27}\text{H}_{26}\text{O}_4$	414.50	78.24 78.19	6.32 6.23

spectra of the novel esters are shown in Fig. 3. The signals characteristic for aromatic skeletal absorption are clearly visible. The vibrations at 3,027–3,081 cm^{-1} which describes the stretching vibrations (ν) of $\text{C}_{\text{Ar}}\text{--H}$ groups, two signals at 1,448–1,494 cm^{-1} and at 1,577–1,598 cm^{-1} connecting with the stretching vibrations (ν) of $\text{C}=\text{C}$ in phenyl ring and very intensive bands in the range of 650–900 cm^{-1} responsible for out-of-plane deformation vibrations (δ) of $\text{C}_{\text{Ar}}\text{--H}$ groups are observed. The signals of the stretching vibrations (ν) of non-aromatic $\text{C}=\text{C}$ groups are found at 1,665 cm^{-1} as a small band. Another characteristic absorption bands for alkenes such as the stretching vibrations (ν) of $=\text{C}\text{--H}$ groups as well as the out-of-plane deformation vibrations (δ) of $=\text{C}\text{--H}$ groups at $-\text{CH}=\text{CH}-$ are overlapping with those characteristic for phenyl ring and thus they are visible in the almost same spectral range. The signals from the aliphatic units are present in the range of 2,849–2,935 cm^{-1} (stretching vibrations ν of $\text{C}\text{--H}$) and at 1,448 cm^{-1} (deformation vibrations δ of $\text{C}\text{--H}$ in $-\text{CH}_2-$ groups) which are partially overlapped with those characteristic for aromatic units. A very intensive absorption peak of the carbonyl group ($\nu \text{C}=\text{O}$) in α, β -unsaturated, aromatic esters is present at 1,720–1,725 cm^{-1} . The lines visible at 1,126–1,176 cm^{-1} and the lines at 1,016–1,070 cm^{-1} are the result of the stretching vibrations (ν) of $\text{C}\text{--O}$ groups in esters. Also, the signals in the range of 1,350–1,385 cm^{-1} characteristic for deformation vibration (δ) of $\text{C}\text{--H}$ for ester compounds appear on the spectrum. The presence of bands at 964 cm^{-1} is directly connected with the skeletal vibrations of $\text{C}\text{--C}$ for cycloalkane and cycloalkene functional groups or out-of-plane deformation vibrations (δ) of $=\text{C}\text{--H}$ for $-\text{CH}=\text{CH}-$ groups. The lack of the absorption bands responsible for the stretching vibrations (ν) of $-\text{OH}$ groups at 3,265 cm^{-1} [28] is the indication that the esterification process was successful and allowed obtaining the compounds which are not previously described in the literature data.

Fig. 3 ATR-FTIR spectra of newly obtained compounds

Fig. 4 ^1H NMR spectra of newly obtained compounds

Fig. 5 ^{13}C NMR spectra of newly obtained compounds

Table 2 Properties of newly obtained compounds

Compound	Viscosity/m Pas	Density/g dm ⁻³	n_D^{20}	$T_{\text{boil}}/^{\circ}\text{C}$
1	885	1.212	1.4955	220
2	725	1.156	1.4870	200
3	890	1.179	1.4920	215
4	950	1.225	1.4910	210

Figures 4 and 5 show the ^1H and ^{13}C NMR spectra of novel compounds, respectively. The resonance signals responsible for the protons at aromatic rings in the range of $\delta = 7.20\text{--}7.90$ ppm are observed. The resonance signals characteristic for the protons assigned to carbon–carbon double bonds: $\delta = 6.30\text{--}6.40$ ppm and $\delta = 6.55\text{--}6.65$ ppm are present. The signals at $\delta = 4.75$ ppm are characteristic for methylene groups in esters. In addition, for compound number 2, the protons attached to cyclohexane rings at 2.90 ppm (protons near carbonyl groups), at 1.80–2.10 ppm, and 1.40–1.50 ppm are clearly visible. The protons in surroundings of carbon–carbon double bonds in cyclohexene ring are observed at 5.70 ppm for compound number 3. The other protons in cyclohexene ring are appeared at 3.10 ppm (protons near carbonyl groups) and at 2.30–2.40 ppm and 2.60–2.70 ppm. In the case of compound number 4, the protons in surroundings of carbon–carbon double bonds in bicyclo ring are appeared at 6.30 ppm and they are partially covered with those characteristic for carbon–carbon double bonds in the side chain. The other protons in bicyclo ring are visible at 3.15–3.30 ppm, 1.60–1.80, and 1.30–1.50 ppm. In addition, the absence of resonance signals characteristic for methylene protons in 3-phenylprop-2-en-1-ol at 4.30 ppm confirms the formation of desired products.

The all resonance signals responsible for the carbons in the structure of those compounds are marked in Fig. 5. In addition, the absence of the signals for carbon in $-\text{CH}_2-$ group of 3-phenylprop-2-en-1-ol (at 64 ppm) and the

Table 3 DSC data of cyclo-aromatic diesters

diester	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{peak (exo)}}/^{\circ}\text{C}$	$T_{\text{peak (endo)}}/^{\circ}\text{C}$
1	280	324	355/395
2	272	320	346/393
3	263	302	319/383
4	244	292	331/396

presence of new signals at 67 ppm (carbons in $-\text{CH}_2-$ groups) and at 175 ppm (carbons in carbonyl groups) confirms the formation of ester products.

The newly obtained compounds are viscous liquids with balsamic odor and boiling temperatures ranges from 200 to 220 $^{\circ}\text{C}$. Their physical properties are placed in Table 2.

Thermal studies

Figure 6 shows the DSC curves of newly obtained compounds. In addition, the DSC data are placed in Table 3. The first DSC signal is exothermic. It appears at temperature over 240 $^{\circ}\text{C}$ with onset temperature (T_{onset}) and peak maximum temperature ($T_{\text{peak (exo)}}$) given in Table 3. The presence of this signal was unexpected because DSC analysis was performed in inert atmosphere. Due to this the decomposition of those compounds should be described by endothermic process. The exothermic signal on DSC curves is connected with the chemical reactions happened during heating of studied compounds. Probably, it is a result of the polymerization process in a gaseous phase of decomposition products formed during heating of studied compounds. This peak is followed by non-well separated endothermic signals with peak maximum temperature ($T_{\text{peak (endo)}}$), Table 3. The presence of those endothermic signals is connected with the main decomposition step of studied compounds.

Fig. 6 DSC curves of newly obtained compounds

Fig. 7 TG and DTG curves of newly obtained compounds

The TG and DTG curves are presented in Fig. 7. In addition, the characteristic data obtained from TG/DTG curves are placed in Table 4. The newly obtained cycloaromatic diesters are compounds with high thermal stability. The initial decomposition temperature determined at 5 % of mass loss (IDT) was higher than 200 °C, Table 4.

In addition, the changes in the degradation path of studied compounds are observed from TG/DTG results. The compound containing phthalic unit (number 1) and compound containing cyclohexane unit (number 2) in the structure decompose in one main step. This decomposition step is appeared as a one non-well separated signal in DTG curves. It occurred from c.a. 200 °C up to temperatures over 450 °C with the significant mass loss above 97 % for compound 1 and above 98 % for compound 2. However, the decomposition of the compound containing cyclohexene unit (number 3) and compound containing nadic unit (number 4) in the structure run through two main steps. The first, non-well separated step is visible from IDT to almost

480 °C with the mass loss over 84 % for compound 3 and over 82 % for compound 4. The second decomposition step is observed at considerably higher temperatures (over 480 °C) with $T_{\max 2}$ 574 °C for compound number 3 and 654 °C for compound number 4 with the mass loss 14.85 % (compound 3) and 8.56 % (compound 4). The presence of this signal is not detected for compound containing phthalic and compound containing cycloalkane units (number 1 and 2).

The analysis of the gaseous products emitted during pyrolysis of studied esters indicates on the similar mechanism of their decomposition at the first step. The FTIR spectra of the gases evolved during the first step of decomposition are gathered at three different temperatures (as three scans), Fig. 8. The first FTIR spectrum was gathered for temperature, where 20 % of mass loss ($T_{20 \%}$) was observed (first scan—a). The second FTIR spectrum was collected where first peak maximum temperature ($T_{\max 1}$) on DTG curves was visible (second scan—b). The

Table 4 TG-DTG data of cyclo-aromatic diesters

diester	IDT/°C	T ₁₀ %/°C	T ₂₀ %/°C	T ₅₀ %/°C	T _{max1} /T _{max1'} /°C	W _{loss1} /%	T _{max2} /°C	W _{loss2} /%	RM/%
1	237	256	278	315	320/376	97.09	—	—	2.91
2	209	243	282	318	321/375	98.04	—	—	1.96
3	236	259	279	316	295/373	84.40	574	14.85	0.75
4	220	251	281	359	293/380	82.90	654	8.56	8.54

RM—residual mass at 700 °C

W_{loss}—mass loss**Fig. 8** FTIR spectra of the gaseous products evolved during the first decomposition step, the spectra gathered at *a*—T₂₀ %, *b*—at T_{max1}, *c*—at T_{max1'}

third FTIR spectrum was obtained for temperature c.a. 373–380 °C where the hump on the first DTG signal was indicated. This temperature was marked as T_{max1'} (third scan—c), Table 4.

The FTIR spectra for all four cyclo-aromatic compounds exhibited bands characteristic for carbon dioxide at 670 cm⁻¹ and 2,310–2,358 cm⁻¹, carbon monoxide at

2,182 and 2,110 cm⁻¹ and water or acids (the region of 3,600–3,700 cm⁻¹) [29–32].

In addition, for all studied compounds, the bands attributed to the aliphatic fragments (stretching vibrations of C–H in –CH₂– groups) at 2,860–2,923 cm⁻¹ are observed. The presence of the stretching vibrations of =C–H and out-of-plane deformation vibrations of =C–H groups

Fig. 8 continued

which appears as bands in the region of $660\text{--}900\text{ cm}^{-1}$ and as two bands at $3,029$ and at $3,081\text{ cm}^{-1}$ characteristic for alkene is indicated. The absorption signals at $3,029\text{--}3,081\text{ cm}^{-1}$ and at $660\text{--}900\text{ cm}^{-1}$ may also be the result of the stretching vibrations of $\text{C}_{\text{Ar}}\text{--H}$ and out-of-plane deformation vibrations of $\text{C}_{\text{Ar}}\text{--H}$. The presence of the stretching vibrations of $\text{C}=\text{C}$ in phenyl rings at $1,440\text{--}1,598\text{ cm}^{-1}$ and in-plane deformation vibrations of aromatic $=\text{C}\text{--H}$ groups for monosubstituted benzenes at $1,146\text{--}1,200\text{ cm}^{-1}$ also indicates the formation of aromatic compounds over the gases emitted during the first decomposition step.

At $T_{20}\%$ and $T_{\text{max}1}$, the presence of the absorption bands at $1,708\text{ cm}^{-1}$ (compound 1 and compound 2) at $1,727\text{ cm}^{-1}$ (compound 3) and at $1,722\text{ cm}^{-1}$ (compound 4)

characteristic for the stretching vibrations of $\text{C}=\text{O}$ groups is observed. The appearance of the peak in the carbonyl region and the bands at $2,710$ and at $2,820\text{ cm}^{-1}$ (stretching vibrations of $\text{C}\text{--H}$ in $\text{O}=\text{C}\text{--H}$ groups) and stretching vibration of $\text{C}\text{--O}$ bond at $1,146\text{ cm}^{-1}$ may indicate on the formation of aldehyde fragments during decomposition of all cyclo-aromatic compounds. In addition, the presence of two bands at $1,806$ and $1,860\text{ cm}^{-1}$ (compound 1 and compound 2), at $1,805$ and $1,862\text{ cm}^{-1}$ (compound 3) and at $1,803$ and $1,847\text{ cm}^{-1}$ (compound 4) responsible for the stretching vibrations of $\text{C}=\text{O}$ groups and at 912 , $1,050\text{--}1,300\text{ cm}^{-1}$ (stretching vibrations of $\text{C}\text{--O}\text{--C}$) suggests the formation of an acid anhydride during decomposition process of newly obtained cyclo-aromatic compounds. The FTIR data clearly indicated that the mixture of various gaseous products was

Scheme 1 The scheme of pyrolysis of studied compounds **Fig. 9** FTIR spectra of the gaseous products evolved during the second decomposition step ($T_{\max 2}$)

evolved during the first decomposition step of studied compounds. Those results suggest that in the temperature range $T_{20\%} - T_{\max 1'}$ as main decomposition products alkene, aromatic, aldehyde, acid and cyclic anhydride fragments are emitted. The results indicate mainly on the *cis* eliminations reaction of diesters during their pyrolysis. It is in accordance with the literature data. Generally, the heating of esters with β -hydrogen causes the cleavage of their bonds and the formation of corresponding alkene and acid fragments [33–35]. However, the emission of carbon dioxide and water indicates also on the partial decarboxylation process of dicarboxylic acids and the formation of corresponding monoacids as well as on the additional condensation reactions of carboxyl groups which can cause the production of acid anhydrides or aldehyde fragments, Scheme 1.

The FTIR spectra of gases evolved during the second decomposition step for all studied compounds are presented in Fig. 9. The spectra confirm that compound containing phthalic unit and compound containing cyclohexane unit (compound 1 and compound 2) in the structure decompose in only one step. At higher temperatures no gases are emitted. However, the FTIR spectra gathered at second peak maximum temperature ($T_{\max 2}$) for compound containing tetrahydrophthalic unit and compound containing nadic unit in the structure are demonstrated only the emission of carbon dioxide and water vapor during the second decomposition step. The existence of the vibrations for carbon dioxide (670 and 2,310–2,358 cm^{-1}) and water (3,600–3,700 cm^{-1}) is detected. It indicates on the carbonization process of the residue formed after the first decomposition step. In addition, the higher residual mass

(8.54 %) at the temperature of 700 °C for compound 4 comparing to other studied compounds is observed, Table 4. Probably, the residue formed after the first decomposition step of compound 4 is more resistant to the carbonization process than residue formed from other compounds. Thus, the carbonization process runs slowly and requires higher temperatures to obtain the total carbonization of the residue formed from compound 4.

Conclusions

TG studies proved that the prepared compounds are characterized by high thermal stability with initial decomposition temperature higher than 200 °C. Dependent on the structure of cyclo-aromatic compounds their thermal decomposition in inert atmosphere run as one or two non-separated steps visible as the peaks in $T_{\max 1}$ and $T_{\max 2}$ on DTG curves. The formation of various compounds during pyrolysis was confirmed by TG/FTIR. The emission of carbon dioxide, carbon monoxide, water vapor, alkene, aromatic, aldehyde, acids, and cyclic anhydrides fragments indicated mainly on the *cis* elimination reactions, partial decarboxylation, and condensation process of carboxyl groups of primary formed decomposition products during pyrolysis.

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