Study on the alcoholysis of aromatic polyesters and related esters using a high-pressure calorimeter

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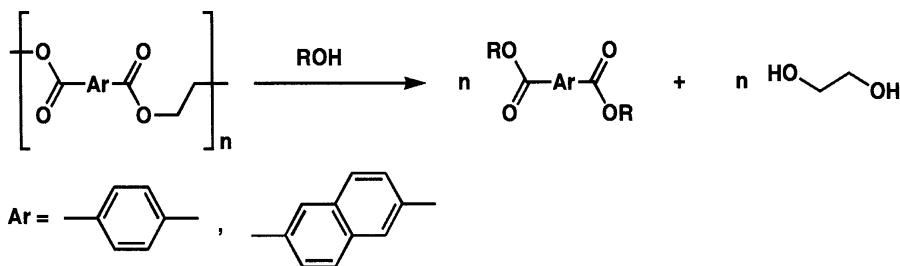
Summary

The heat of base-catalyzed alcoholysis of poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) as well as several related aromatic and aliphatic esters has been measured using a high-pressure calorimeter. The process is essentially thermoneutral, and heats of CH_3ONa-catalyzed methanolysis of PET and PEN are + 1.8±0.6 and +9.3±0.2 kJ/mol-carboxyl group, respectively. Furthermore, the heats of $Zn(OCOCH_3)_2$-catalyzed alcoholysis of PET with ethylene glycol and benzyl alcohol are also calculated as +5.8±0.2 and +6.6±0.8 kJ/mol-carboxyl group, respectively. These values are comparable to those for ethyl esters of *p*-substituted benzoic acids and propionic acid.

Introduction

Recycling of poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) wastes is one of emerging problems in the field of plastic industry in recent years (1). As a recycling method, much attention has been paid to the degradation of the waste resins to their monomers, which includes the alcoholysis (Scheme 1) (2) and the hydrolysis (3) under sub- or supercritical conditions. These technologies have an advantage of large reaction rate even in the absence of any catalysts. To our surprise, however, there are no report of the thermochemical studies on the alcoholysis and hydrolysis of these polymers at high temperatures and pressures. Thermodynamic data of all stages of industrial process is indispensable to elaborate optimal conditions of the procedure. Thus, we attempted to measure the heat of alco-

Scheme 1. Alcoholysis of aromatic polyesters.

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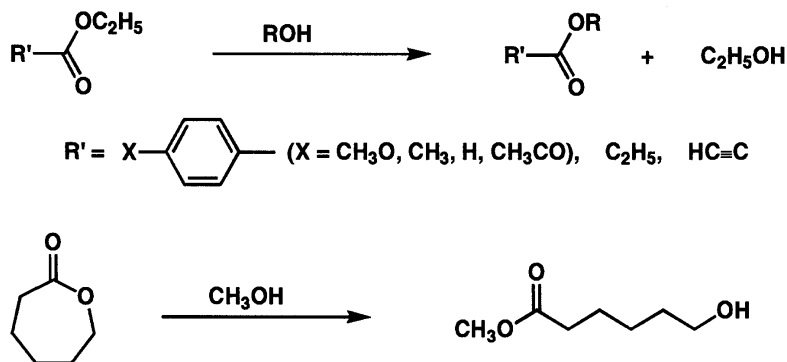
Scheme 2. Alcoholysis of aromatic and aliphatic esters.

holysis of PET and PEN using methanol, benzyl alcohol and ethylene glycol as an alcohol. As a comparison, alcoholysis of several related esters (Scheme 2) was also studied at high temperatures and pressures.

Experimental

Reagents

Poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) were purchased from Aldrich as pellets and used after grinding to powder (diameter; PET,< 0.5 mm: PEN, <0.25 mm). Ethyl benzoate (EB), ethyl *p*-methoxybenzoate (EMeOB), ethyl *p*-methylbenzoate (EMeB), ethyl *p*-acetylbenzoate (EAcB), ethyl propionate (EPN), ethyl propiolate (EPL), ε-caprolactone (CL) were purchased from Wako Pure Chemicals (all guaranteed reagents) and used without further purification. Methanol, benzyl alcohol and ethylene glycol (Wako Pure Chemicals, all guaranteed reagents) were dried over molecular sieves 4A for at least two days. Solid CH_3ONa (Wako Pure Chemicals) and anhydrous $Zn(OCOCH_3)_2$ (Aldrich) were used as received.

Apparatus and Procedure

High-pressure calorimetric measurement of the alcoholysis was carried out on a Tian-Calvet type SETARAM C80II calorimeter, which was calibrated by carrying out the measurement of the heat of fusion of tin (literature value: +7.03 kJ/mol (4)). The objective heat flow-temperature profile was obtained by subtracting the heat flow-temperature profile for pure alcohol from that for the ester/alcohol system.

The conversion of the starting materials was determined by gravimetry, gas chromatography (Shimadzu GC-14B equiped with a capillary column (Spelco SPB-1, 30 m)) or ^1H NMR spectroscopy (Varian UNITY-INOVA-400) of the reaction mixture.

Results and Discussion

The alcoholysis of the esters performed in this study was very clean, and nearly quantitative except the ethyl *p*-acetylbenzoate/methanol (without any catalyst) system. The analysis of the reaction mixture showed that any other degradation products could not

Table 1. Heat of alcoholysis of *p*-substituted benzoic acid ethyl esters [a]

entry	ester	alcohol	heat of reaction (kJ/mol)
1	EMeOB	CH_3OH	+21.6±0.5
2	EMeB	CH_3OH	+9.8±0.6
3	EB	CH_3OH	+3.4±0.9 (1.7 [b])
4	EAcB	CH_3OH	+7.4±0.3 (4.8 [c])
5	EB	$HOCH_2CH_2OH$	+1.6±0.7
6 [d]	EB	$C_6H_5CH_2OH$	+3.1±1.5

[a] Conditions: [ester]$_o$/[alcohol]$_o$ = 1/40.3; alcohol, 4mL.   [b] In the presence of CH_3ONa (5 mol%).   [c] In the presence of $Zn(OCOCH_3)_2$ (5 mol%).   [d] [EB]$_o$/[alcohol]$_o$ = 1/15.8; alcohol, 4mL.

be detected within the experimental error, consistently with the report on the methanolysis of PET by Sako et al. (2). The heat of alcoholysis of several ethyl esters of *p*-substituted benzoic acid, aliphatic carboxylic acids and polyesters are summarized in Table 1, Table 2 and Table 3, respectively.

Alcoholysis of Ethyl Benzoate, Its Derivatives and Aliphatic Esters

First of all, we studied the methanolysis of low-molecular-weight ethyl esters. In methanolysis, an endothermic peak was always observed at ca 240 °C, which sometimes disturbed the estimation of the heat of reaction. When methanol solution of toluene or methyl benzoate (0.22-1.15 M) was heated, an analogous endothermic output was observed, the position and the area of which were slightly dependent upon the nature and the amount of the solute. Considering the critical temperature of methanol (239.5 °C (5)), the endothermic peak is thought to stem from the difference between the heat capacity of methanol and those of the methanol/solute systems near critical point.

Under our conditions, the methanolysis of ethyl benzoate (EB), ethyl *p*-methoxybenzoate (EMeOB), ethyl *p*-methylbenzoate (EMeB) and ethyl *p*-acetylbenzoate (EAcB) proceeded homogeneously throughout the reaction. Table 1 lists the heats of methanolysis ($\Delta H_{methanol}$) of the esters, and the relationship between the $\Delta H_{methanol}$ obtained here and the Hammett's substituent constant (σ_p) (6) are shown in Fig. 1. In regard to the kinetics of transesterification, Gassman et al. found that the linear free energy relationship for the methanolysis of 1-phenylcyclohexyl benzoates at 50 °C, and they reported the reaction constant (ρ) of +1.37 (7). Very recently, Gagne et al. reported the ρ value of +2.35 for the alkali metal *tert*-butoxide-catalyzed transesterification of methyl benzoates and ethyl acetate (8). In contrast, any clear correlation between the $\Delta H_{methanol}$ and the σ_p value was not found in our study. Guthrie et al. reported a similar tendency for the heat of aminolysis of *p*-substituted methyl benzoates with dimethylamine in methanol (9). For ethyl propionate (EPN), the $\Delta H_{methanol}$ of +3.2±1.7 kJ/mol was determined, which is comparable to values for benzoic acid derivatives. Thus, it can be concluded that the methanolysis of the esters is essentially thermoneutral, whether the esters are derived from aliphatic carboxylic acids or from aromatic carboxylic acids.
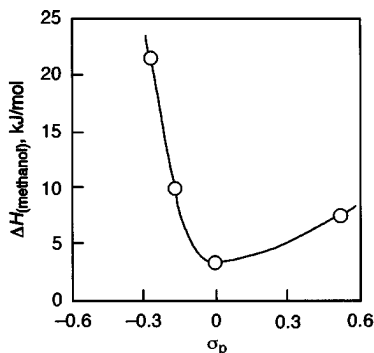
Figure 1.   Relationship between σ_p and $\Delta H_{\text{methanol}}$ of ethyl esters of *p*-substituted benzoic acids.

Judging from the $\Delta H_{\text{methanol}}$s for EB and EAcB, the presence of a catalyst (CH_3ONa or $Zn(OCOCH_3)_2$) scarcely affected $\Delta H_{\text{methanol}}$.

The reaction of ε-caprolactone (CL) with methanol cleanly gave methyl 6-hydroxyhexanoate by heating to 180 °C. The $\Delta H_{\text{methanol}}$ of CL of -18.2±0.4 kJ/mol was obtained. The heat of bulk polymerization of CL catalyzed by $Ti(O\text{-}n\text{-}C_4H_9)_4$ at 150 °C has been reported as -18.6 - -22.6 kJ/mol (10). The $\Delta H_{\text{methanol}}$ of CL obtained in this study was comparable to this value, probably suggesting that, like the case of the polymerization, the release of the ring strain is a main driving force of the methanolysis. We believe that this, in turn, is suggestive of the thermoneutrality of the ester exchange process itself. When ethyl propiolate (EPL) was heated in methanol to 230 °C, a large exotherm of -56.8 kJ/mol was observed due to the concurrent oligomerization of EPL.

Alcoholysis of EB with benzyl alcohol or ethylene glycol was seemingly slower than the methanolysis under our conditions. The heat of alcoholysis with benzyl alcohol ($\Delta H_{\text{benzyl alcohol}}$) and ethylene glycol ($\Delta H_{\text{glycol}}$) for EB were +3.1±1.5 kJ/mol and +1.6 ±0.7 kJ/mol, respectively (Table 1).

Alcoholysis of Aromatic Polyesters

In order to complete the reaction below ca 240 °C and to avoid the superposition of some thermal outputs over the objective heat flow, the use of a catalyst was inevitable.

Table 2.   Heat of methanolysis of aliphatic esters [a]

entry	ester (mmol)	heat of reaction (kJ/mol)
1	EPN (2.77)	+3.2±1.7
2	EPL (3.00)	−56.8 [b]
3	CL (2.45)	−18.2±0.4

[a] Conditions: $[\text{ester}]_o/[\text{alcohol}]_o = 1/40.3$; alcohol, 4mL.   [b] Oligomerization of the ester concurrently took place.

Table 3. Heat of alcoholysis of aromatic polyesters[a]

entry	polyester	alcohol	additive	heat of reaction (kJ/mol)
1	PET	CH_3OH	CH_3ONa	$+1.8 \pm 0.6$
2	PET	$HOCH_2CH_2OH$	$Zn(OCOCH_3)_2$	$+5.8 \pm 0.2$
3	PET	$C_6H_5CH_2OH$	$Zn(OCOCH_3)_2$	$+6.6 \pm 0.8$
4	PEN	CH_3OH	CH_3ONa	$+9.3 \pm 0.2$

[a] Conditions: [repeating unit of the polyesters]$_o$/[alcohol]$_o$ = 1/49.4; alcohol, 4 mL; additive, 10 mol%.

The methanolysis of PET in the presence of catalytic amount of CH_3ONa (10 mol% of the repeating units) completed below 160 °C, from which the $\Delta H_{methanol}$ of 1.8±0.6 kJ/mol-carboxyl group was determined (Table 3). This $\Delta H_{methanol}$ value is somewhat smaller than that for ethyl p-acetylbenzoate, when σ_p values for p-CH_3CO- (+0.52) (6) and p-C_2H_5OCO- (+0.52) (6) are considered.

PEN was also cleanly and quantitatively depolymerized in methanol to dimethyl 2,6-naphthalenedicarboxylate and ethylene glycol by heating up to 290 °C without any catalysts or by heating up to 210 °C in the presence of CH_3ONa (10 mol% of the repeating units). The $\Delta H_{methanol}$ of PEN in the presence of CH_3ONa was calculated to be +9.3±0.2 kJ/mol-carboxyl group, as listed in Table 3. This value is somewhat larger than the $\Delta H_{methanol}$ for PET, but is within the range expected from the results for ethyl esters of substituted benzoic acids (Table 1).

Precise estimation of the heat of uncatalyzed alcoholysis of PET with ethylene glycol or benzyl alcohol was impossible because of overlapping of the heat of dissolution of unreacted PET on the heat flow due to the alcoholysis. For PET, the ΔH_{glycol} and the $\Delta H_{benzyl\ alcohol}$ in the presence of $Zn(OCOCH_3)_2$[11] (10 mol% of the repeating units) were +5.8±0.2 and +6.6±0.8 kJ/mol-carboxyl group. These results show that the heat of alcoholysis of PET is virtually independent of the kind of alcohol.

References.

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1. (a) Datye KV, Raje HM, Sharma ND (1984) Resources and Conservation 11: 117 (b) Baliga S, Wong WT (1989) J Polym Sci, Part A, Polym Chem 27: 2071

2. Sako T, Sugeta T, Otake K, Nakazawa N, Sato M, Namiki K, Tsugumi M (1997) J Chem Eng Jpn 30: 342

3. Ajiri M, Sato O, Machida K, Saito I, Arai K (1997) Kagakukougaku Ronbunshu 23: 505

4. Speros DM, Woodhouse RL (1964) J Phys Chem 67: 2164

5. Lide DR (ed) (1996) Handbook of Chemistry and Physics, 76th Ed pp 6-57. CRC Press, Boca Raton, FL

6. (a) Jaffé HH (1953) Chem Rev 53: 191 (b) Brown HC, Okamoto Y (1957) J Am Chem Soc 79: 1915

7. (a) Gassman PG, Hartman GD (1972) J Chem Soc, Chem Commun: 853 (b) Gassman PG Hartman GD (1973) J Amer Chem Soc 95: 449

8. Stanton MG, Allen CB, Kissling RM, Lincoln AL, Gagne MR (1998) J Am Chem Soc 120: 5981

9. Guthrie JP, Pike DC, Lee Y-C (1992) Can J Chem 72: 1671

10. Rafler G, Bonatz E (1993) Angew Makromol Chem 229: 199

11. Grunschke H, Hammerschick W, Naucheim B (1968) U.S. Patent 3,404,115