

THERMOGRAVIMETRIC EXAMINATION OF POLYALCOHOL-FORMATE BINARY SYSTEMS

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Abstract

Mixtures of trimethylolpropane (TMP) or pentaerythritol (PER) with sodium or calcium formate (SF or CF) were investigated all over their composition range.

Complete additivity was found to occur in the case of the TMP-SF and TMP-CF systems which renders it possible to determine the contents of both TMP and the given formate from independent signals of weight loss over the entire range of quantitative composition of the mixtures under investigation.

Additivity was found not to occur in the PER-SF system in the entire range of quantitative composition; SF content could only be determined from the ash weight.

In the PER-CF system, additivity was absent at some signals; CF content could be determined in the full range from three independent signals, PER could be determined independently only at its content up to 50% by weight.

Keywords: polyalcohol-formate binary system, TG

Introduction

Mixtures of trimethylolpropane (TMP) or pentaerythritol (PER) with sodium formate (SF) or calcium formate (CF) were investigated. The mixtures are models for the process streams formed during manufacturing of the above polyalcohols from formaldehyde and butyric or acetic aldehyde, respectively, using sodium or calcium hydroxide both as a catalyst and a reacting substance to fix formic radicals [1-3].

The thermal properties of the components of the subject mixtures are well known. The compounds, specifically formates, have been thermally analyzed and the results published many times [e.g. 4-7]. However, the behaviour of their mixtures has not been described.

The purpose of the present work was to investigate the behaviour of polyalcohol-formate mixtures comprising various concentrations of their components, with a view to developing thermogravimetric methods to analyze the compositions of the above streams. To begin with, the properties of the mixtures

were checked for additivity in relation to the properties of their individual components.

Experimental

Materials

Trimethylolpropane from Perstorp, pentaerythritol from Fluka and sodium formate from POCh, all the analytical grade, were used. Calcium formate was obtained by neutralizing pure 85% formic acid with pure calcium carbonate.

Thermogravimetry

The Mettler TA 4000/TG-50 thermobalance was used. Thermogravimetric measurements were performed at the following parameters:

- weigh of the samples 10–12 mg,
- dynamic air atmosphere ($200 \text{ ml}\cdot\text{min}^{-1}$),
- open cylindrical Pt crucible,
- heating rate $12 \text{ deg}\cdot\text{min}^{-1}$ (from ambient temperature to 850°C).

The powdered components of the mixtures were weighed and placed in the crucible at proper ratios, beginning with the one present at a smaller quantity in the mixture.

Results and discussion

TG curves of the compounds under examination (obtained at the assumed measurement conditions) are shown in Fig. 1. The curves convey information

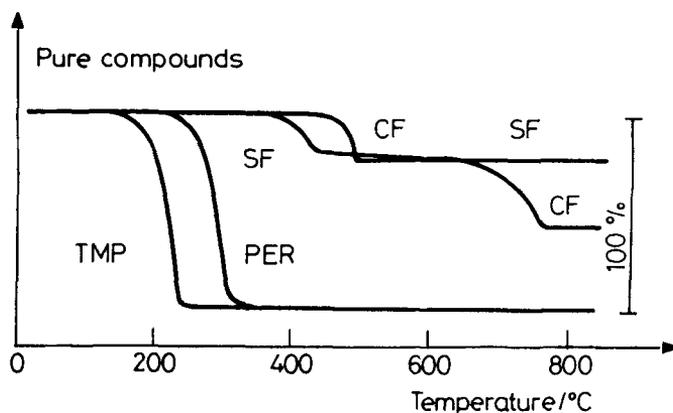


Fig. 1 TG curves of pure compounds: TMP, PER, SF and CF

Table 1 Thermogravimetric behaviour of pure compounds

Compound	Source transformation	TG signal		Denotation of source in mixtures	
		Source information	Theoretical value / %wt		Experimental value / %wt
TMP	vaporisation	Δm_{30}^{250}	100.0	99.31	Δm_1
PER	vaporisation with	Δm_{30}^{330}	100.0	96.49	Δm_1
	thermal decomposition	Δm_{50}^{500}	100.0	99.82	—
SF	HCOONa	m_{250}	100.0	99.83	m_1
	$2\text{HCOONa} \rightarrow \text{Na}_2\text{CO}_3 + \dots$	Δm_{800}^{250}	22.06	21.48	Δm_{2-4}
	Na_2CO_3	m_{800}	77.94	78.02	m_4
	$(\text{HCOO})_2\text{Ca}$	m_{300}	100.00	99.90	m_1
CF	$(\text{HCOO})_2\text{Ca} \rightarrow \text{CaCO}_3 + \dots$	Δm_{300}^{550}	23.08	23.04	Δm_2
	CaCO_3	m_{550}	76.92	76.76	m_2
	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	Δm_{800}^{800}	33.85	33.83	Δm_3
	CaO	m_{800}	43.08	42.74	m_3

about the course of the following well known chemical conversions of the compounds:

- when melted, at $T_f \cong 58\text{--}60^\circ\text{C}$, TMP evaporates,
- when melted, at $T_f \cong 258\text{--}260^\circ\text{C}$, PER evaporates and decomposes to volatiles and small amounts of carbonized compounds which then burn,
- when melted, at $T_f \cong 251\text{--}253^\circ\text{C}$, sodium formate decomposes to finally produce sodium carbonate,
- solid calcium formate decomposes to calcium carbonate which then decomposes to calcium oxide.

The above thermal decomposition reactions proceed quantitatively (Table 1), which makes their TG data useful as analytical signals.

Polyalcohol-formate mixtures were examined in the full range of their quantitative composition; measurement points were condensed at the range boundaries. Examples of TG/DTG curves of the mixtures are shown in Fig. 2. Upon analysis of the shape of the TG and DTG curves obtained, the following TG data were selected and tested as analytical signals:

TMP – SF: Δm_1 for TMP; m_1 , Δm_{2-4} , m_4 for SF,

TMP – CF: Δm_1 for TMP; m_1 , Δm_2 , m_2 , Δm_3 , m_3 for CF,

PER – SF: m_4 for SF,

PER – CF: Δm_1 for PER; Δm_2 , m_2 , Δm_3 , m_3 for CF.

Regression lines, $Y = a + bX$, of the content of a given component, as calculated from TG data (Y) vs. its known content (X) in the mixture, have then been evaluated for all the selected signals. The results are shown in Table 2.

As it was found in all the cases that the intercept (a) was close enough to 0, slope (b) close enough to 1 and correlation coefficient was not smaller than 0.998, the following conclusions were drawn:

- for TMP–SF and TMP–CF, all signals obtainable could be regarded as analytical ones;
- for PER–SF, only the weight of the residue (ash) could be regarded as an analytical signal;
- for PER–CF, Δm_1 and Δm_2 could be treated as analytical signals only in the case of mixtures containing less than 50% by weight of PER, the other ones, namely m_2 , Δm_3 and m_3 are analytical signals all over the range of quantitative composition of the mixtures.

Disturbances in the quantitative course of evaporation, or evaporation with decomposition to volatiles, of PER from the mixtures with formates are probably caused by the catalytic effect of formates on the thermal decomposition of PER to carbonized products. A feature of PER carbonization which can be identified by the TG method is the occurrence of steps Δm_{1a} and Δm_4 (Fig. 2).

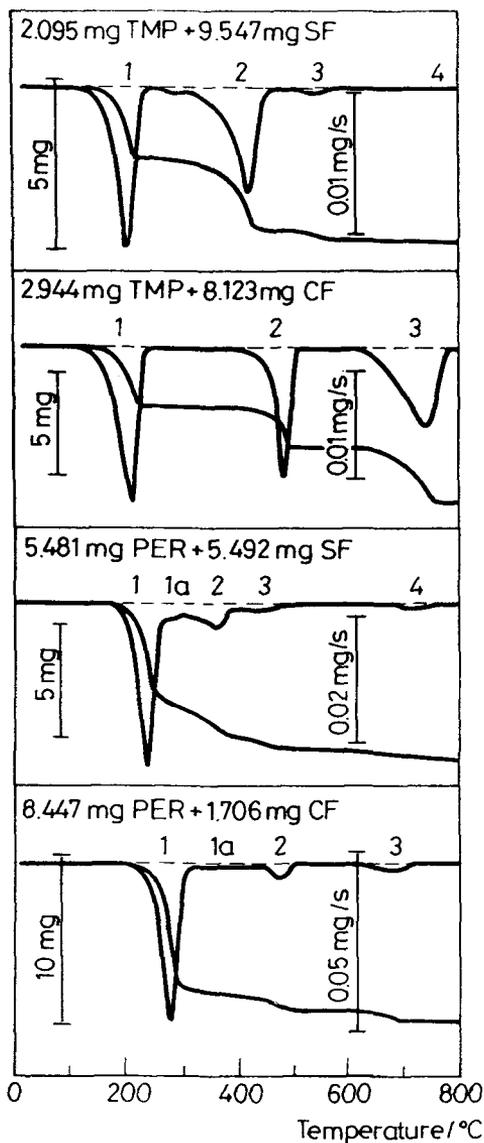


Fig. 2 Examples of TG and DTG curves of binary mixtures

Standard estimation error has been established as definitely smaller than 1% by weight in all the cases under examination. This permits a presumption that quantitative determination of components in mixtures is feasible and can be accurate in the range of concentration of each component in the binary mixtures, that is roughly 1–99% by weight [8].

Table 2 Results of correlation analysis

Binary system	Content of compound	Source	Analytical factor	Content as determined ($Y = a + bX$)		Std. error of estim. / %wt
				a / %wt	b	
TMP-SF	WTMP	Δm_1	1.000	0.0013	0.9973	0.19
	WSF	m_1	1.000	0.2732	0.9972	0.20
	WSF	Δm_{2-4}	4.533	-0.7510	0.9949	0.51
	WSF	m_4	1.283	0.4994	0.9945	0.30
TMP-CF	WTMP	Δm_1	1.000	0.2540	0.9916	0.14
	WCF	m_1	1.000	0.5825	0.9917	0.15
	WCF	Δm_2	4.333	0.5533	0.9971	0.76
	WCF	m_2	1.300	0.4035	0.9927	0.43
	WCF	Δm_3	2.955	-0.4056	0.9970	0.51
	WCF	m_3	2.321	0.4898	0.9917	0.68
PER-SF	WPER	100-(m_4)	-	0.1943	0.9988	0.57
	WSF	m_4	1.283	-0.0774	0.9988	0.57
PER-CF	WPER	Δm_1	1.000	-0.0305	0.9988	0.05
	< 50 %					
	WCF	Δm_2	4.333	0.0016	0.9849	0.41
> 50 %	WCF	m_2	1.300	0.2400	1.0022	0.17
	WCF	Δm_3	2.955	-0.2554	0.9948	0.16
	WCF	m_3	2.321	0.4847	1.0079	0.40

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Zusammenfassung — Gemische aus Trimethylolpropan (TMP) oder Pentaerythritol (PER) mit Natrium- oder Calciumformiat (SF oder CF) wurden im gesamten Konzentrationsbereich untersucht.

Im Falle der Systeme TMP-SF und TMP-CF wurde volle Additivität festgestellt, was es ermöglicht, anhand unabhängiger Gewichtsverlustsignale im gesamten Bereich der quantitativen Zusammensetzung der untersuchten Gemische den Gehalt von sowohl TMP als auch des betreffenden Formiates zu bestimmen.

Beim PER-SF-System konnte im gesamten Bereich der quantitativen Zusammensetzung keine Additivität festgestellt werden; der SF-Gehalt kann ausschließlich anhand des Aschegewichtes ermittelt werden.

Im PER-CF-System fehlt die Additivität bei einigen Signalen; der CF-Gehalt kann im vollen Bereich von drei unabhängigen Signalen bestimmt werden, PER kann jedoch unabhängig nur bis zu einem Gehalt bis zu 50 Gew% ermittelt werden.