



ELSEVIER

Thermochimica Acta 324 (1998) 33–48

thermochimica
acta

A comparison of the thermal decomposition of preservatives, using thermogravimetry and rising temperature kinetics

David Dollimore^{*}, Carolyn O'Connell

Department of Chemistry, University of Toledo, 2801 W. Bancroft St., Toledo, OH 43606-3390, USA

Abstract

The thermal behaviors of benzoic, sorbic and citric acids, which are three commonly used preservatives, were studied by thermogravimetry. The kinetic mechanisms of evaporation and/or decomposition in air and nitrogen were determined and compared. Benzoic acid completely evaporated via a zero-order kinetic mechanism. Sorbic acid partially evaporated by a zero-order kinetic mechanism, with the production of a transition compound. Citric acid decomposed to a transition compound by a combination of kinetic mechanisms. A majority of the process followed zero-order kinetic principles, with the evaporation of most of the sample. The activation energies of evaporation and the pre-exponential terms were calculated and compared. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Arrhenius parameters; Evaporation; Preservatives; Rising temperature kinetics; Thermogravimetry

1. Introduction

Chemical preservatives are commonly added to food products to decrease or eliminate the growth of food-borne pathogens, assuring a longer shelf life. Many foods contain two or more different preservatives to maximize the antimicrobial action and minimize adverse effects from high concentrations of a single preservative. Most food products are subjected to thermal treatment during processing, storage and preparation. When heated, the preservatives may go through a phase transition and then evaporate, or they may degrade, either from the solid or the liquid state. The purpose of this study is to examine the behavior of preservatives during heating, using thermogravimetry to determine the kinetics of evaporation and/or decomposition.

Evaporation is the transition from the liquid phase to the vapor phase, without a change in chemical composition. Evaporation is dependent on the vapor pressure of the substance, molecular weight, temperature and the amount of exposed surface area. The main factor influencing the evaporation of a preservative is temperature.

A decomposition reaction is defined as a chemical process in which a reactant is degraded into a simpler species. Decomposition reactions include processes in which the crystal lattice structure is destroyed, such as melting, sublimation and evaporation, as well as chemical reactions, resulting in the formation of a new compound [1]. In solid-state decomposition, the transformation occurs in an area with enhanced reactivity, referred to as the reaction interface or the boundary between the reactant and the product [1]. The decomposition of a substance can be described on the basis of chemical kinetic principles. Many decomposition reactions are treated as zero-order, first-order or pseudo-first-order reactions. In solid-state reactions,

^{*}Corresponding author. Tel.: +1-419-5302109; fax: +1-419-530-4033; e-mail: ddollim@uoft02.utoledo.edu

concentration is not monitored, as it is in conventional chemical kinetic studies, because it does not vary in a manner that can be correlated with changes in the quantity of the remaining reactants [1]. Instead, the fraction reacted (α) is determined.

Evaporation can be monitored by determining the rate of mass loss as a substance undergoes the phase transition from liquid to vapor. This is achieved by using thermogravimetry, with a rising temperature program [2]. The data obtained from the TGA curve of mass vs. temperature or time is converted into a DTG plot, where the rate of mass loss (dm/dt) is measured against temperature or time, in this study. A preliminary kinetic mechanism can then be assigned from the shape of the DTG plot. In the case of a zero-order reaction, the DTG plot shows a maximum value for dm/dt at the point where the mass of material is exhausted, so that the return of dm/dt to the baseline of zero is very abrupt. The fraction evaporated, α , is calculated, using Eq. (1):

$$\alpha = (m_i - m_t)/(m_i - m_f) \quad (1)$$

where m_i and m_f are the initial and final masses in milligrams, respectively [2]. The mass at the specific time is represented by m_t . The data points are obtained from the curved portion of the DTG plot [3]. A plot of α vs. time or temperature yields a sigmoidal-shaped curve. If evaporation is occurring, the fraction evaporated is the product of the time and the coefficient of evaporation, k_{vap} , i.e.:

$$\alpha = k_{\text{vap}}t \quad (2)$$

At constant temperature, k is equal to $d\alpha/dt$ [2]. The rate of evaporation is given by dm/dt . For zero-order reactions, the coefficient of evaporation can be calculated by dividing dm/dt by the cross sectional area of the sample crucible. The coefficient of evaporation may be dependent on the gas-flow rate. It may also depend on the particle size, if sublimation takes place. However, in the present study, the evaporation occurs from a liquid interface, where a zero-order mechanism would be expected. When $\ln k_{\text{vap}}$ is plotted against $1/T$ (Kelvin temperature), a straight line is obtained, with a slope equal to E_{vap}/R , where E_{vap} is the activation energy of evaporation and R the gas constant. Such plots are consistent with the Arrhenius equation:

$$k_{\text{vap}} = A e^{-E_{\text{vap}}/RT} \quad (3)$$

or

$$\ln k_{\text{vap}} = \ln A_{\text{vap}} - E_{\text{vap}}/RT \quad (4)$$

which also allows the determination of the pre-exponential term, A_{vap} [4]. For other decomposition mechanisms, the results can be correlated to a set of models, which are based on nucleation, diffusion, reaction order or geometrical factors of the reactant-product interface [4]. In solid-state decomposition, the reaction rate is given by:

$$d\alpha/dt = kf(\alpha) \quad (5)$$

where $f(\alpha)$ is a function of α and t the time [5]. This can be related to the temperature by:

$$d\alpha/dT \equiv d\alpha/dt \times dt/dT = [kf(\alpha)]/\beta \quad (6)$$

where β is the heating rate, in degrees per second [6]. Eq. (6) can then be written in the form:

$$k = [(d\alpha/dT)\beta]/f(\alpha) \quad (7)$$

The term $f(\alpha)$ can be obtained from tables of different mechanisms. For first-order mechanisms, it is equal to $(1-\alpha)$ [5]. Using the Arrhenius method:

$$\ln [(d\alpha/dT)\beta/f(\alpha)] = \ln A - E/RT \quad (8)$$

A plot of $\ln [(d\alpha/dT)\beta]/f(\alpha)$ vs. $1/T$ can be used to determine the Arrhenius parameters. Table 1 contains a summary of the various $f(\alpha)$ expressions used in this study [4].

In the present study, benzoic acid, citric acid and sorbic acid, which are preservatives used in food

Table 1
Solid-state rate expressions for deceleratory α -time curves [4]

	$g(\alpha)=kt$	$f(\alpha)=(1/k)(d\alpha/dt)$
<i>Geometrical models</i>		
R2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
R3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
<i>Diffusion mechanisms</i>		
D1	α^2	$1/2\alpha$
D2	$(1-\alpha) \ln(1-\alpha) + \alpha$	$[-\ln(1-\alpha)]^{-1}$
D3	$[1-(1-\alpha)^{1/3}]^2$	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
D4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$
<i>Reaction order</i>		
F1	$-\ln(1-\alpha)$	$1-\alpha$
F2	$(1-\alpha)^{-1}$	$(1-\alpha)^2$
F3	$(1-\alpha)^{-2}$	$1/2(1-\alpha)^3$

products, are characterized using a simultaneous TGA–DTA unit. As some of these materials evaporate or sublime, the data collected refers to the process of evaporation. The analysis is indicated in the discussion of the results.

2. Experimental

2.1. Reagents

The benzoic acid (C_6H_5COOH) of 99% purity was obtained from Aldrich. It is a white crystalline solid. The sorbic acid ($CH_3-CH=CH-CH=CH-COOH$) was obtained from Sigma, reagent grade. The anhydrous citric acid ($C_6H_8O_7$) was obtained from Fisher Scientific, 99.8% purity. It is a white crystalline material. Citric acid is a tricarboxylic acid, which also contains a hydroxyl group.

2.2. Thermal analysis

The thermal analysis equipment consisted of a simultaneous TGA–DTA unit, TA Instruments Model Number 2960. The experimental data was analyzed using the TA Instruments Thermal Analyst 2000 software, TGA–DTA-1.0, V1.0B. The samples were placed in a platinum crucible, with an empty platinum crucible as a reference. A heating rate of $10^\circ C \text{ min}^{-1}$ was used during all experiments. The samples were analyzed in dry nitrogen and dry air at 100 ml min^{-1} . The gas-flow rate was monitored with an electronic flowmeter. The sample size varied from 5.1 to 11.4 mg. Each run was repeated three times under the same conditions, in order to exclude error. In order to confirm the kinetic mechanism, isothermal runs were completed with the appropriate gas at a flow rate of 100 ml min^{-1} . Each run lasted forty minutes, with ten minutes allowed for temperature equilibration. The isothermal temperature varied with the substance studied. Each isothermal run yielded a linear plot, confirming the kinetic mechanism as zero order.

2.3. Scanning electron microscopy

A sample of anhydrous citric acid was heated to $370^\circ C$ in flowing nitrogen at 100 ml min^{-1} , in a combustion furnace. The system was purged with

nitrogen until the sample reached ambient temperature. A small amount of brown residue was noted after heating. An untreated sample and the heat-treated sample were sprinkled onto double-sided tape, attached to specimen mounts. The samples were sputter-coated with gold/palladium. The samples were examined in a scanning electron microscope at an accelerating potential of 5.0 kV. The samples were viewed by scanning the entire sample and a representative area was photographed at $200\times$ magnification.

3. Results and discussion

3.1. Thermal analysis

Three runs were completed for each preservative, in dry nitrogen and dry air. Consistent results were noted. The temperature vs. time plot showed a linear heating rate at $10^\circ C \text{ min}^{-1}$. Plots of temperature difference vs. temperature and weight percentage vs. temperature were obtained for each sample. Two endotherms, corresponding to melting and evaporation, were observed for each sample. The experimental data is summarized in Table 2.

The benzoic acid had a very slight mass loss at the melting point, which was probably the result of air or water loss from the crystal lattice structure. There was complete mass loss following the melting point, as the sample completely evaporated. The evaporation endotherm had a peak temperature that was $6^\circ C$ higher in air, than in nitrogen. This suggests that oxygen, carbon dioxide or another component in air exerts an inhibitory effect on evaporation. The DTG plot contained two peaks. A very small peak corresponded to mass loss at the melting point, as discussed previously. A large, sharp peak, characteristic of evaporation, corresponded to complete sample loss after the melting point. The melting and evaporation of benzoic acid has been well studied, using several different methods [7–10]. It has been suggested for use as a calibration standard for thermal analytical studies [7,11]. Sample TGA, DTG and DTA plots for benzoic acid heated in nitrogen and air are found in Figs. 1 and 2, respectively.

When sorbic acid was heated in nitrogen, complete evaporation did not occur, as a small amount of amber colored residue ($\approx 0.6\%$) was noted at the end of each

Table 2
Melting and evaporation endotherms of preservatives

Run#	Gas	Benzoic acid		Sorbic acid		Citric acid	
		melt/°C	evap/°C	melt/°C	evap/°C	melt/°C	evap, °C
1	N ₂	123.80	181.49	135.82	173.08	157.20	217.80
2	N ₂	123.80	177.88	135.82	179.09	158.20	220.40
3	N ₂	123.20	186.30	135.58	179.81	157.70	219.20
Mean		123.60	181.89	135.74	177.33	157.70	219.13
1	Air	122.60	186.30	135.58	168.27	157.21	216.35
2	Air	123.80	189.30	135.58	174.04	157.21	226.44
3	Air	123.80	185.70	135.58	163.46	157.20	230.80
Mean		123.40	187.10	135.58	168.59	157.21	224.53

run. The residue is probably a transition compound formed during the decomposition of sorbic acid, which is thermally unstable at temperatures $>100^{\circ}\text{C}$. When the sorbic acid samples were heated in dry air, the melting points remained constant at 135.58°C . The endotherms corresponding to evaporation had an average temperature of 168.59°C , a slightly lower temperature than in nitrogen. This suggests that evaporation occurs more readily in air than in nitrogen. A black residue remained at the end of the runs, which comprised 3–4% of the total sample mass. At the end of the nitrogen runs, only 0.6% of the sample remained. The ΔT signal on the DTA was also lower, -0.12°C , as opposed to -2.46°C in nitrogen. These results suggest that a transition compound forms, when the sample is heated in air before evaporation is complete. Pure, dry sorbic acid is stable at low temperatures. An exothermic event occurred at ca. 308°C , corresponding to combustion of gases released by the degradation of the carbonaceous intermediate. This suggests that the transition compound is heat stable, relative to the sorbic acid, as it did not degrade until after 300°C was reached. Sample TGA, DTG and DTA plots for sorbic acid heated in nitrogen and air are found in Figs. 3 and 4, respectively.

The citric acid heated in dry nitrogen behaved similarly to the other preservatives, with endotherms corresponding to melting and evaporation. A black residue remained after heating to 600°C , comprising ca. 4% of the total sample mass. It is thought that an intermediate compound was formed, which decomposes to a carbonaceous residue with further heating. When the citric acid was heated in air, the melting and evaporation endotherms were unchanged. A large

exotherm was noted at 472°C , followed by almost complete mass loss. The exotherm is the result of the glowing combustion of the solid residue. Representative TGA, DTG and DTA plots for citric acid heated in nitrogen and air are found in Figs. 5 and 6, respectively.

A spreadsheet was used to calculate α for each of the preservatives. Data points were taken at intervals of every 2°C . Plots of α vs. temperature were made. Sigmoidal-shaped curves were noted for all samples, as expected. The rate constants were calculated by dividing dm/dt by the cross-sectional area of the crucible. Table 3 contains representative experimental dm/dt and k_{vap} data for benzoic acid in dry nitrogen. Plots of $\ln k_{\text{vap}}$ vs. $1/T$ were made. A linear plot should be obtained for a zero-order reaction. Fig. 7 contains plots of $\ln k_{\text{vap}}$ vs. $1/T$ for benzoic acid, heated in nitrogen and air. The benzoic acid data yielded linear plots, with regression coefficients very close to unity. The activation energies and pre-exponential terms were determined. The results are summarized in Table 4. As can be observed from the table, the activation energies of the benzoic acid samples varied slightly, when the sample was heated in a different gas.

A linear response was obtained from the sorbic acid samples, when $\ln k_{\text{vap}}$ vs. $1/T$ was plotted, using the zero-order rate constants. Since a product was remaining at the end of the runs, total evaporation did not occur. Therefore, the possibility existed that another kinetic mechanism was taking place during all or part of the decomposition. The spreadsheet was used to calculate the specific rate constants for the first-order, geometrical and diffusion mechanisms, using the expressions summarized in Table 1. When the various

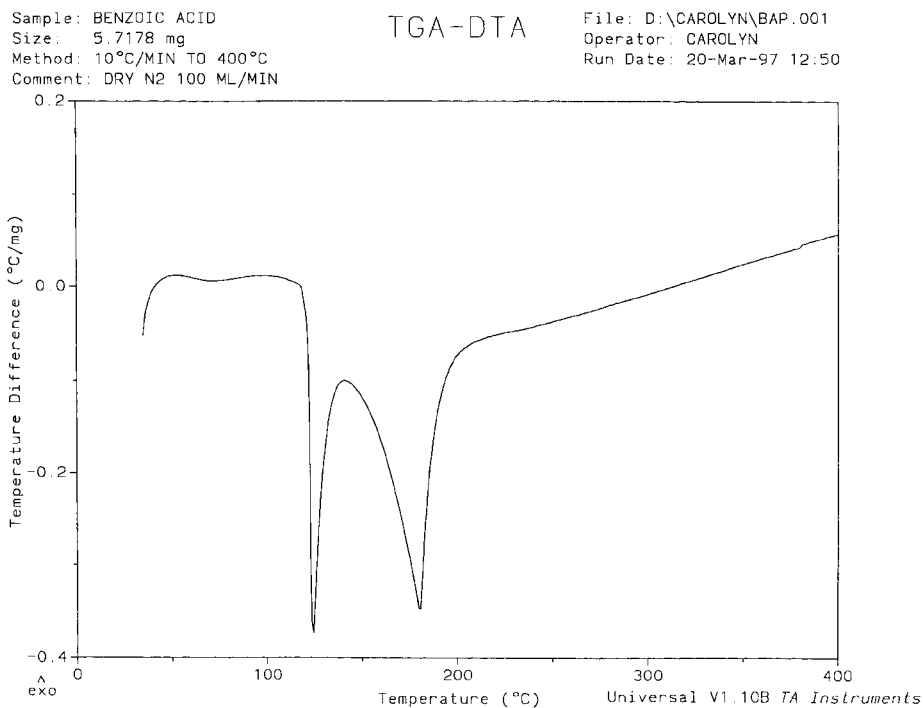
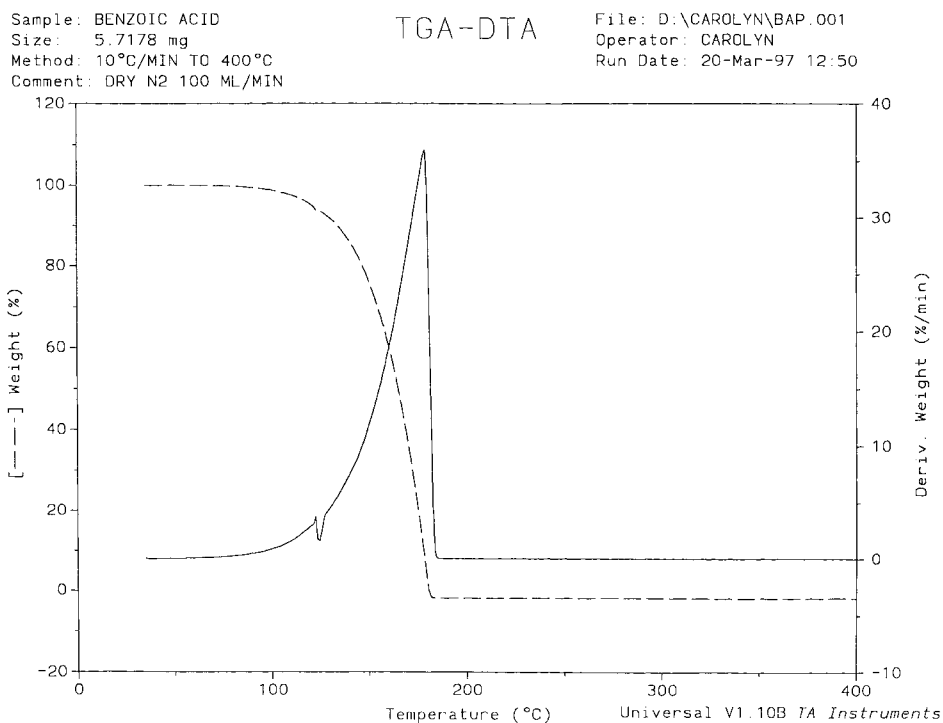
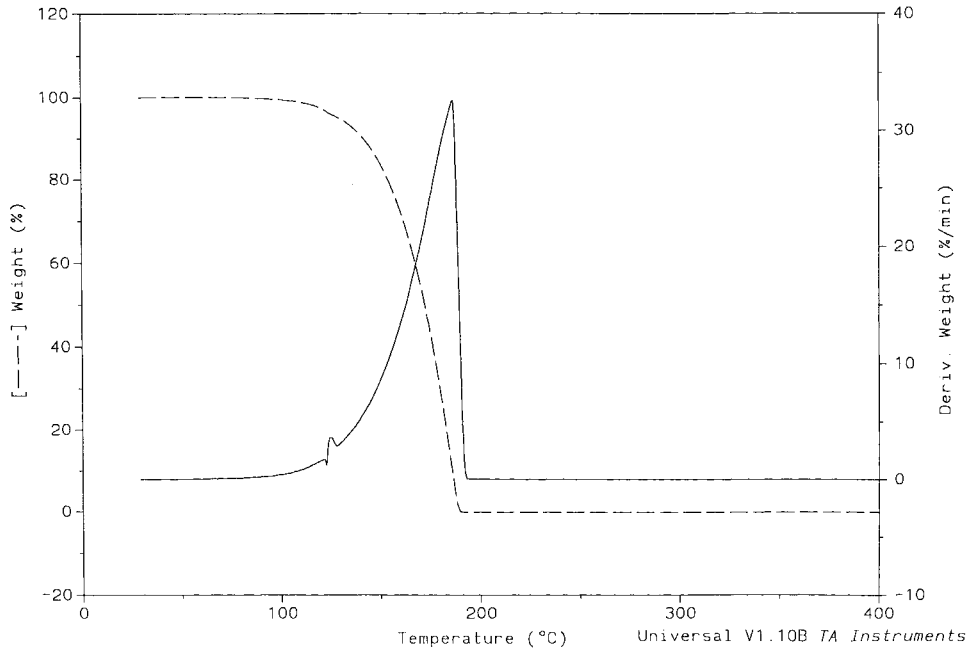


Fig. 1. (a) TGA and DTG plots for benzoic acid in dry nitrogen at 100 ml min⁻¹. (b) DTA plot for benzoic acid in dry nitrogen at 100 ml min⁻¹.

Sample: BENZOIC ACID
 Size: 8.5924 mg
 Method: 10°C/MIN TO 400°C
 Comment: DRY AIR 100 ML/MIN

TGA-DTA

File: D:\CAROLYN\BENZ.01
 Operator: CAROLYN
 Run Date: 17-Jun-97 12:22



Sample: BENZOIC ACID
 Size: 8.5924 mg
 Method: 10°C/MIN TO 400°C
 Comment: DRY AIR 100 ML/MIN

TGA-DTA

File: D:\CAROLYN\BENZ.01
 Operator: CAROLYN
 Run Date: 17-Jun-97 12:22

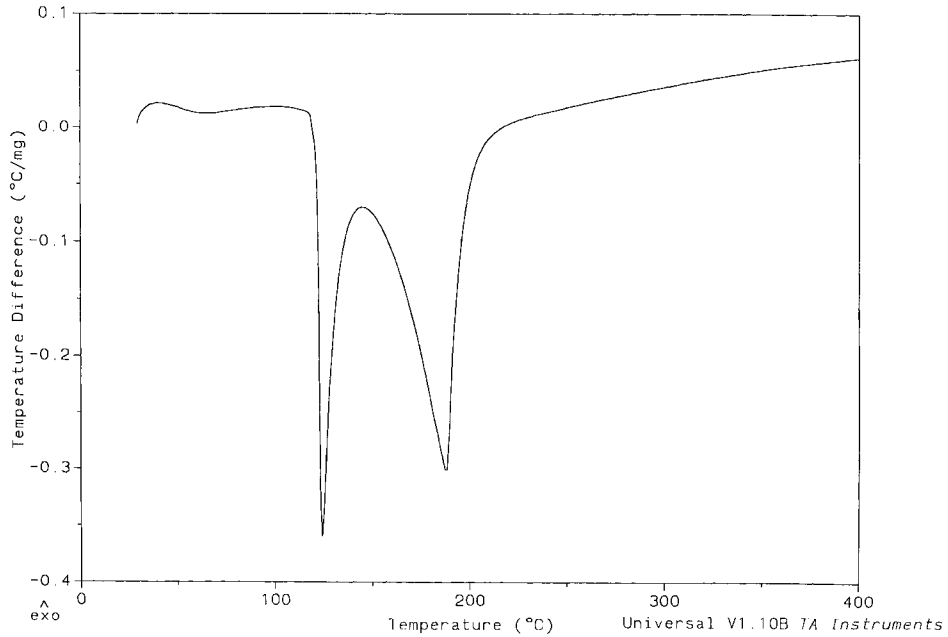


Fig. 2. (a) TGA and DTG plots for benzoic acid in dry air at 100 ml min^{-1} . (b) DTA plot for benzoic acid in dry air at 100 ml min^{-1} .

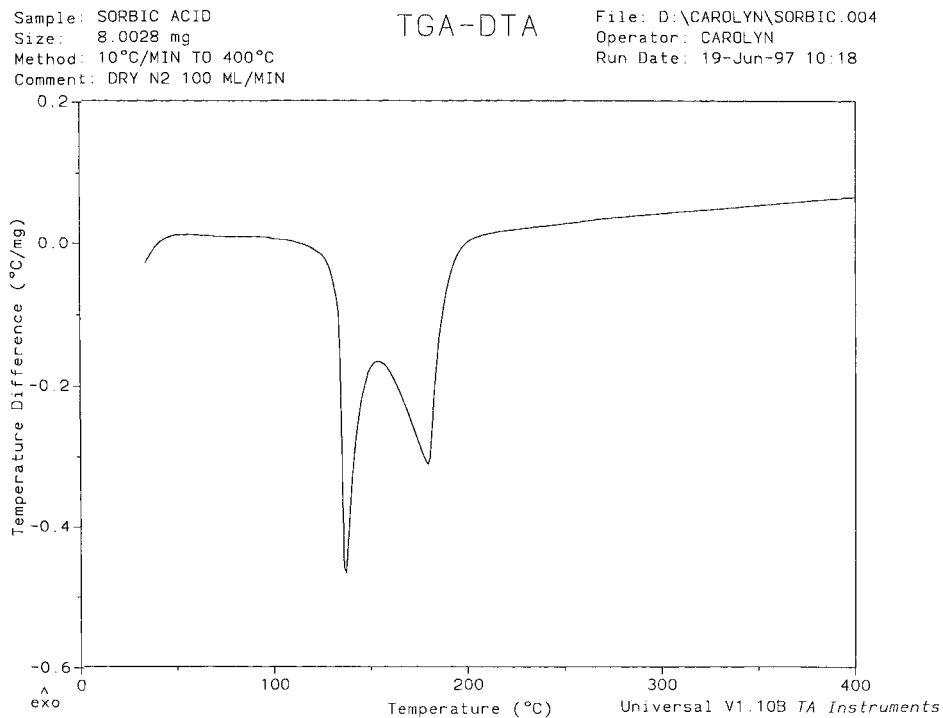
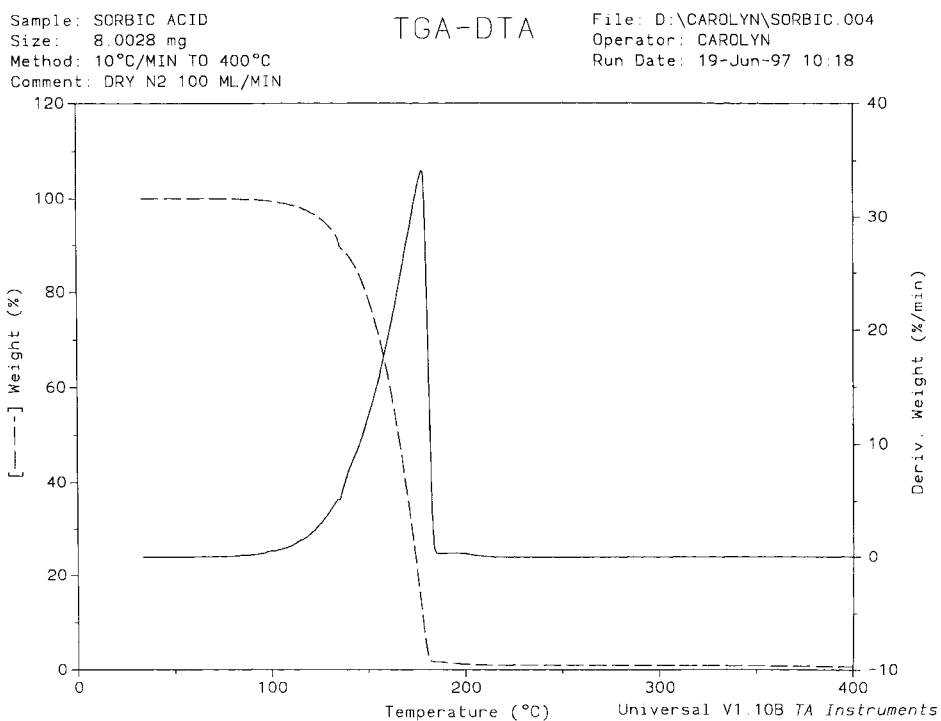
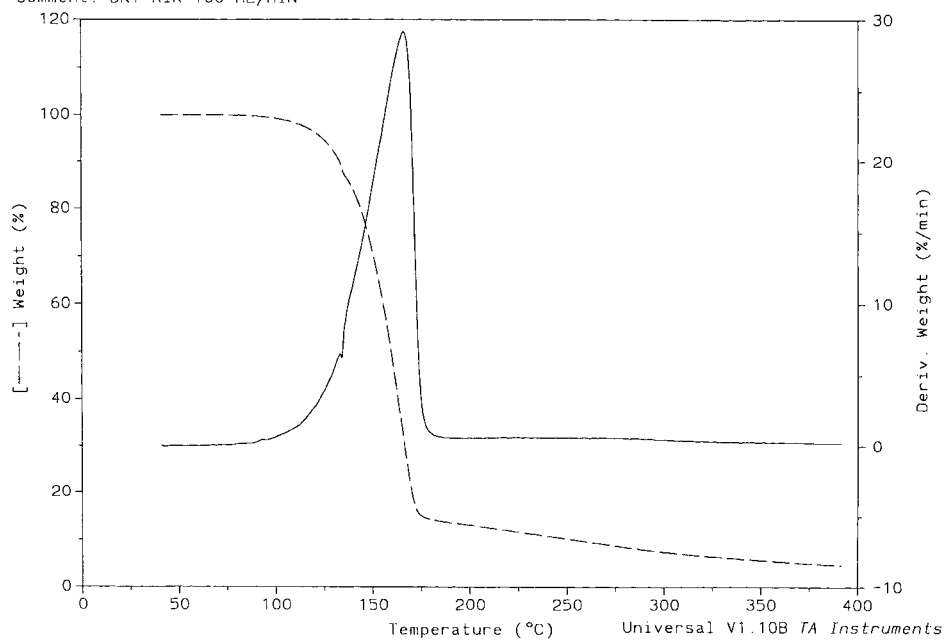


Fig. 3. (a) TGA and DTG plots for sorbic acid in dry nitrogen at 100 ml min⁻¹. (b) DTA plot for sorbic acid in dry nitrogen at 100 ml min⁻¹.

Sample: SORBIC ACID
 Size: 5.6864 mg
 Method: 10°C/MIN TO 400°C
 Comment: DRY AIR 100 ML/MIN

TGA-DTA

File: D:\CAROLYN\SORB.06
 Operator: CAROLYN
 Run Date: 17-Jul-97 12:54



Sample: SORBIC ACID
 Size: 5.6864 mg
 Method: 10°C/MIN TO 400°C
 Comment: DRY AIR 100 ML/MIN

TGA-DTA

File: D:\CAROLYN\SORB.06
 Operator: CAROLYN
 Run Date: 17-Jul-97 12:54

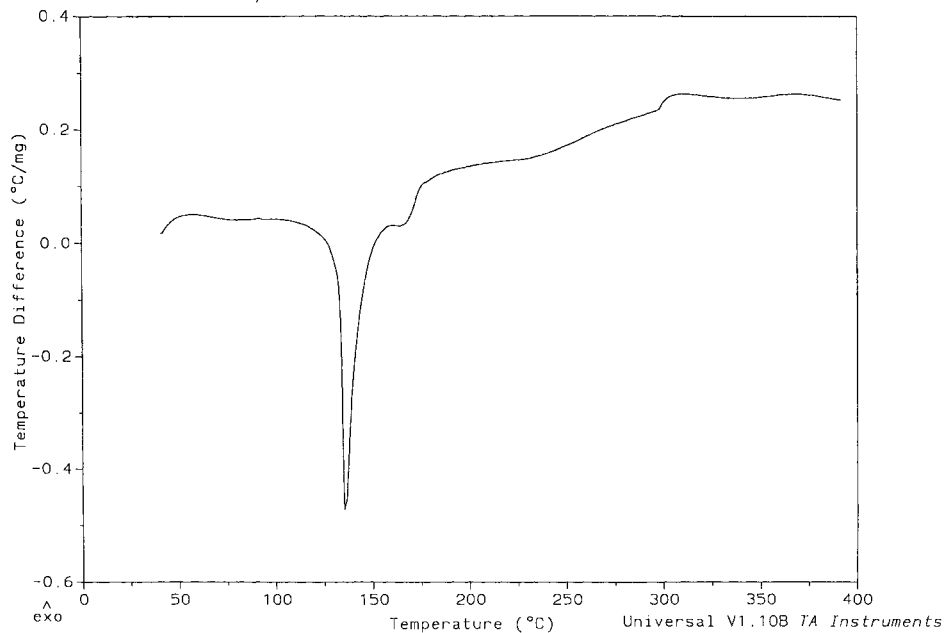
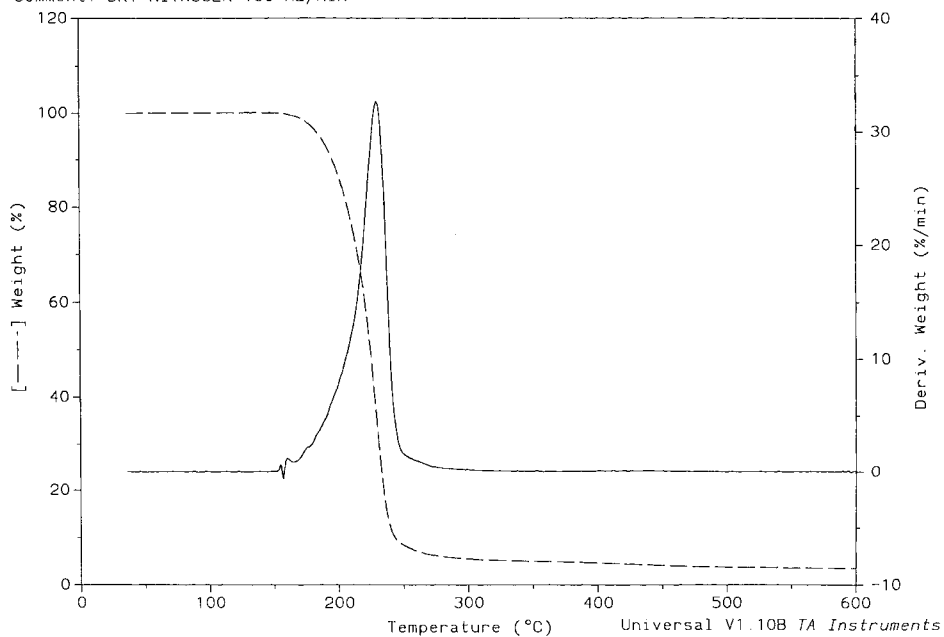


Fig. 4. (a) TGA and DTG plots for sorbic acid in dry air at 100 ml min^{-1} . (b) DTA plot for sorbic acid in dry air at 100 ml min^{-1} .

Sample: CITRIC ACID
 Size: 9.5580 mg
 Method: 10°C/MIN TO 600°C
 Comment: DRY NITROGEN 100 ML/MIN

TGA-DTA

File: D:\CAROLYN\CITRIC.004
 Operator: CAROLYN
 Run Date: 20-Jun-97 13:39



Sample: CITRIC ACID
 Size: 9.5580 mg
 Method: 10°C/MIN TO 600°C
 Comment: DRY NITROGEN 100 ML/MIN

TGA-DTA

File: D:\CAROLYN\CITRIC.004
 Operator: CAROLYN
 Run Date: 20-Jun-97 13:39

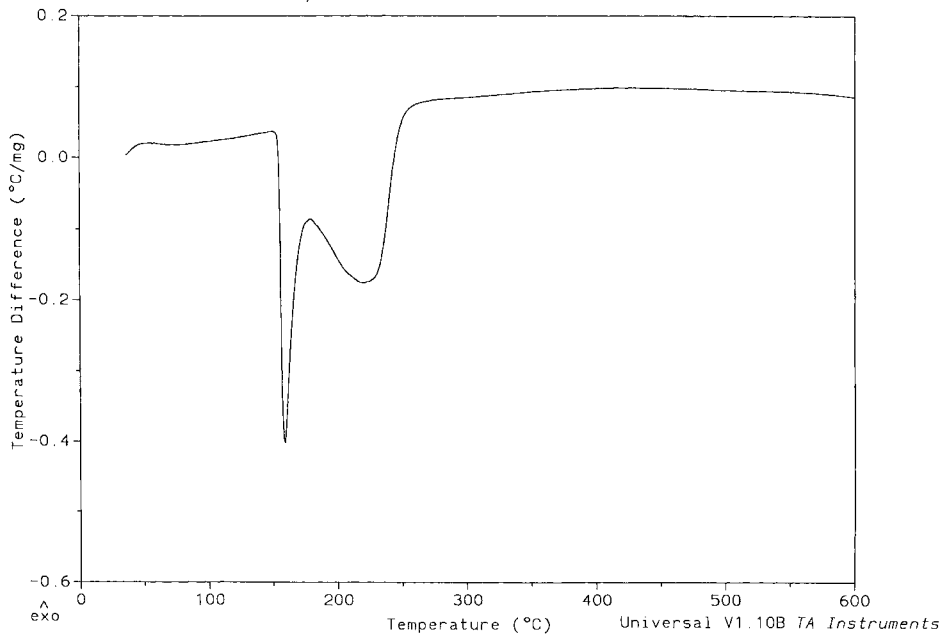


Fig. 5. (a) TGA and DTG plots for citric acid in dry nitrogen at 100 ml min^{-1} . (b) DTA plot for citric acid in dry nitrogen at 100 ml min^{-1} .

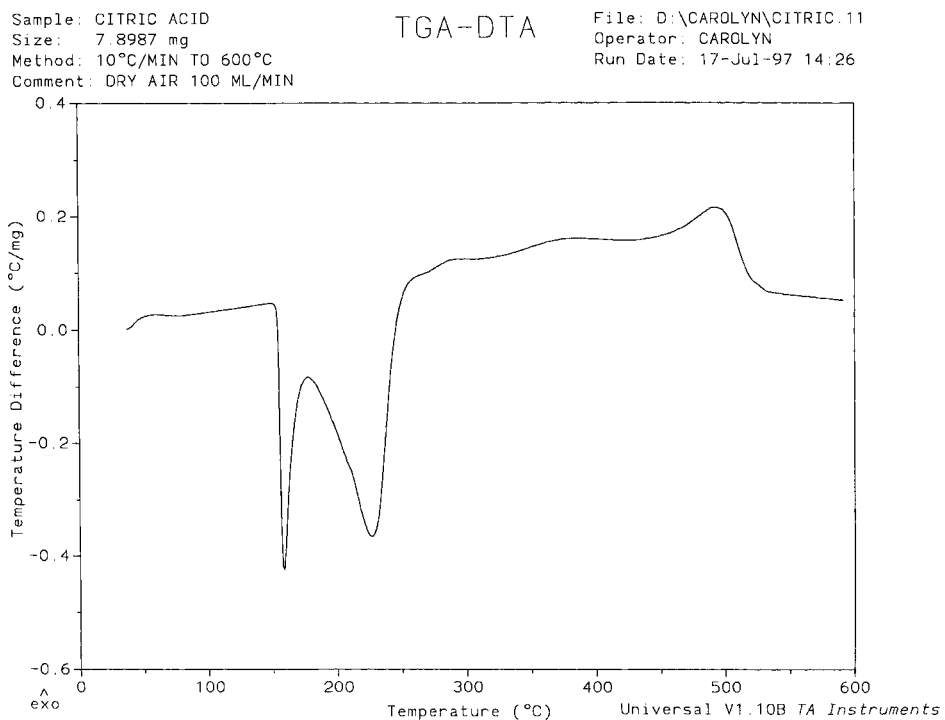
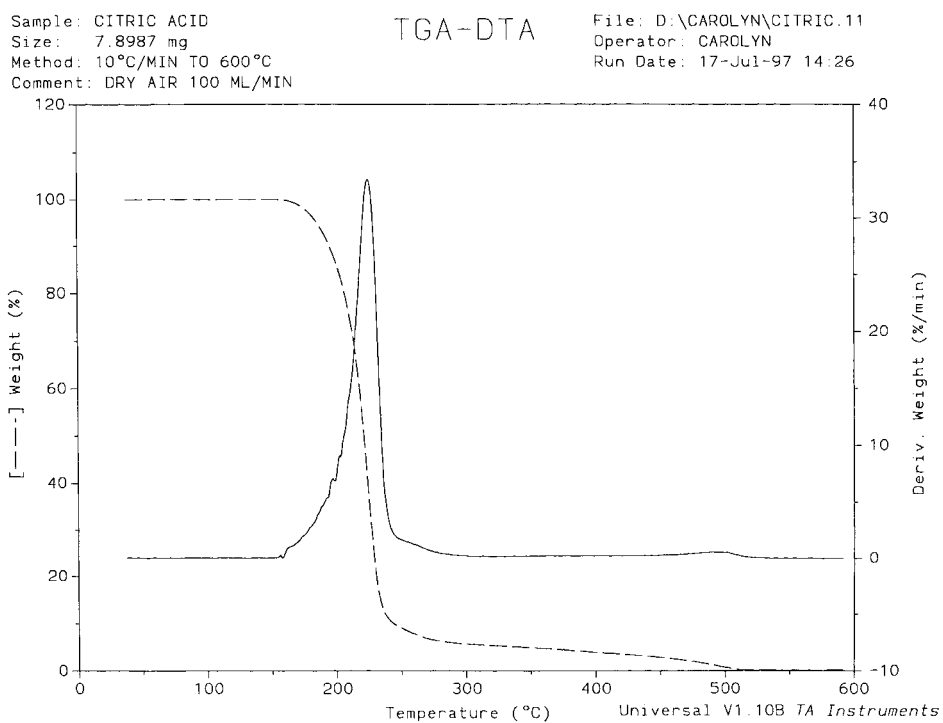


Fig. 6. (a) TGA and DTG plot for citric acid in dry air at 100 ml min^{-1} . (b) DTA plot for citric acid in dry air at 100 ml min^{-1} .

Table 3
Representative dm/dt and k_{vap} data for benzoic acid in nitrogen

Temp/°C	Temp/K	$dm/dt/$ (mg min^{-1})	$k_{\text{vap}}/$ ($\text{mg min}^{-1} \text{cm}^{-2}$)
130	403	0.261	0.885
132	405	0.290	0.984
134	407	0.322	1.091
136	409	0.357	1.211
138	411	0.393	1.332
140	413	0.431	1.461
142	415	0.470	1.594
144	417	0.513	1.739
146	419	0.565	1.914
148	421	0.620	2.102
150	423	0.681	2.308
152	425	0.746	2.527
154	427	0.815	2.761
156	429	0.890	3.016
158	431	0.972	3.293
160	433	1.060	3.592
162	435	1.154	3.911
164	437	1.253	4.246
166	439	1.359	4.605
168	441	1.466	4.968
170	443	1.582	5.361
172	445	1.701	5.764
174	447	1.821	6.171
176	449	1.937	6.564
178	451	2.045	6.930

mechanisms were compared, the zero-order plot of $\ln k_{\text{vap}}$ vs. $1/T$ yielded the regression coefficient closest to unity. Fig. 8 contains the plot of $\ln k_{\text{vap}}$ vs. $1/T$, for sorbic acid heated in nitrogen and air. The plots for the other kinetic mechanisms yielded sigmoidal- or con-

vex-shaped curves, hence it was concluded that a zero-order process was taking place.

A linear response was obtained from the citric acid samples in nitrogen and air, when $\ln k_{\text{vap}}$ vs. $1/T$ was plotted, using the zero-order rate constants. The regression coefficient was not as close to unity, as in the case of benzoic and sorbic acids. All of the citric acid samples exhibited small areas of non-linearity, occurring in the same temperature ranges. This suggests that the decomposition of citric acid may occur by more than a single kinetic mechanism. This is supported by the fact that it does simply evaporate, but a product is produced. Sigmoidal-shaped curves were obtained when the other kinetic expressions listed in Table 1 were plotted. It can be concluded that the decomposition of citric acid occurs via a combination of two or more kinetic mechanisms. The plots of $\ln k_{\text{vap}}$ vs. $1/T$ can be found in Fig. 9.

When the activation energies of the three preservatives are compared, it can be noted that the sorbic acid has the lowest energy of evaporation. The activation energy of benzoic acid is slightly higher, by ca. 2 KJ mol⁻¹. This accounts for the fact that both of these preservatives undergo almost complete evaporation, at fairly low temperatures. This should be considered when using sorbic and benzoic acids as preservatives in cooked or baked products. The activation energy of evaporation of citric acid was much higher than the other two preservatives studied; by ca. 35–37 KJ mol⁻¹. This was expected, as citric acid decomposed by a mechanism different from that of the other preservatives. No significant changes in the activation energies were noted between the samples

Table 4
Arrhenius constants of preservatives

Run #	Gas	Benzoic acid		Sorbic acid		Citric acid	
		$E_{\text{vap}}/$ (KJ mol ⁻¹)	A_{vap}^a	$E_{\text{vap}}/$ (KJ mol ⁻¹)	A_{vap}^a	$E_{\text{vap}}/$ (KJ mol ⁻¹)	A_{vap}^a
1	N ₂	65.79	2.9×10^8	61.19	1.2×10^8	96.40	1.1×10^{11}
2	N ₂	65.95	3.2×10^8	63.11	2.1×10^8	101.30	3.9×10^{11}
3	N ₂	66.49	3.9×10^8	63.22	2.2×10^8	100.91	2.9×10^{11}
Mean		66.07	3.3×10^8	62.51	1.8×10^8	99.54	2.6×10^{11}
1	air	66.64	4.2×10^8	67.70	7.6×10^8	103.80	8.8×10^{11}
2	air	67.50	5.6×10^8	65.09	3.6×10^8	103.83	6.7×10^{11}
3	air	66.94	4.7×10^8	61.73	1.4×10^8	89.75	0.2×10^{11}
Mean		67.03	4.8×10^8	64.84	4.2×10^8	99.12	5.2×10^{11}

^a Units of $\text{mg min}^{-1} \text{cm}^{-2}$.

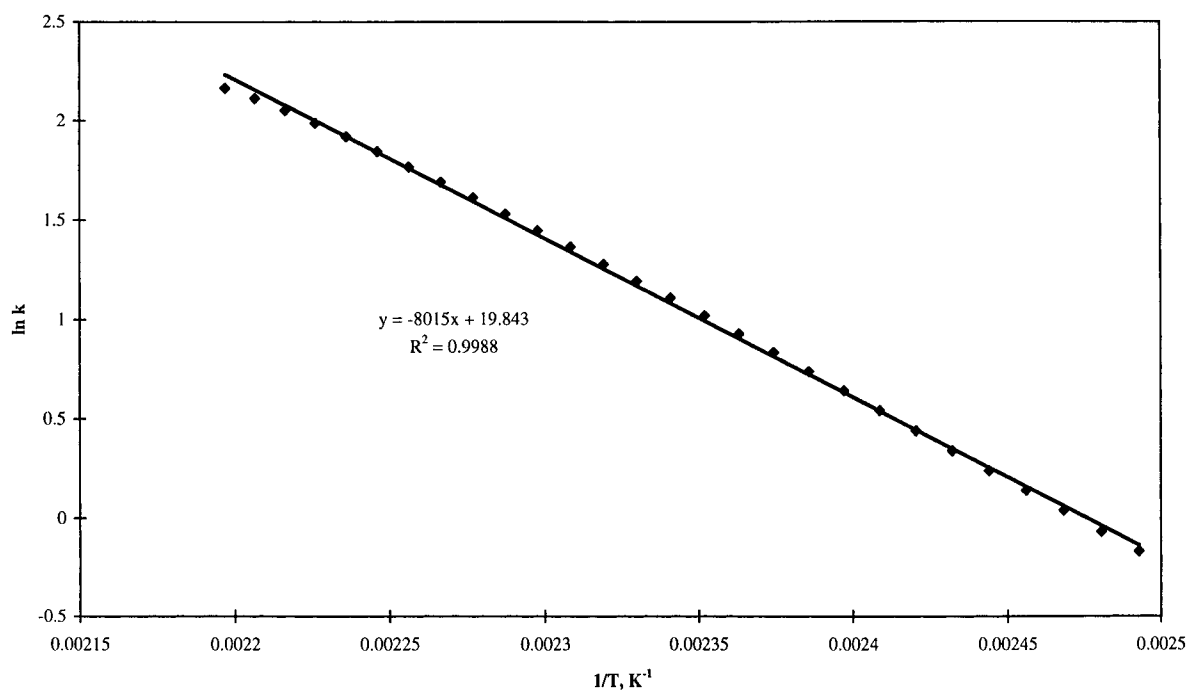
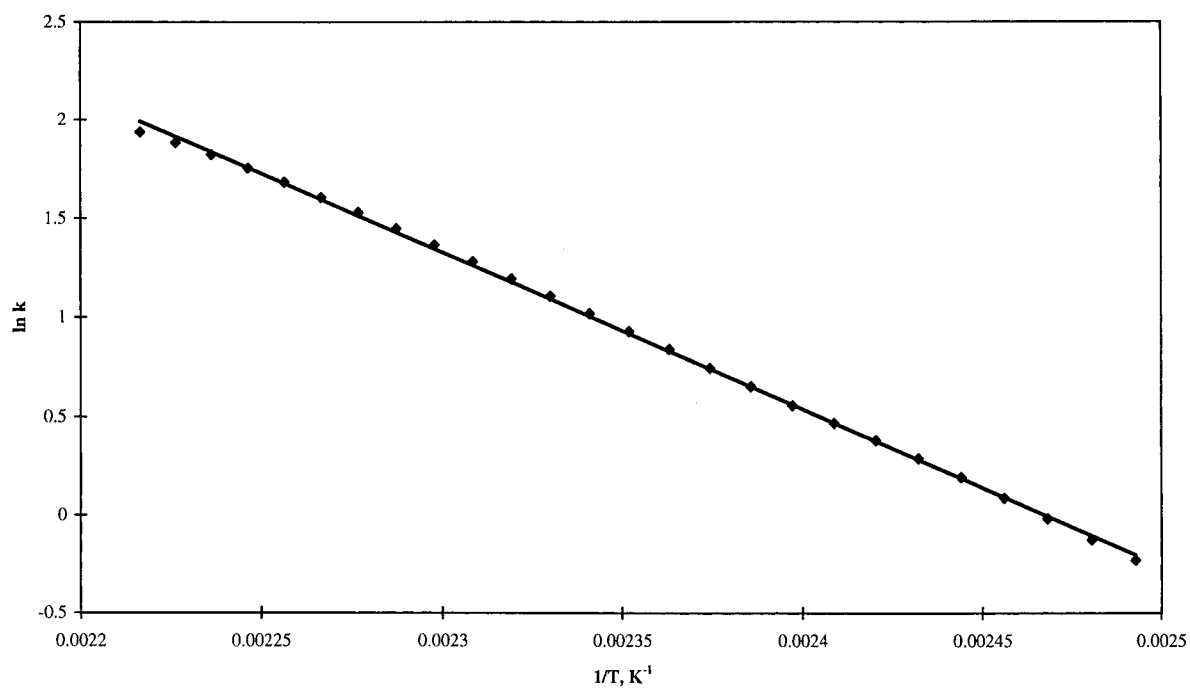


Fig. 7. (a) $\ln k$ (Zero-order) vs. $1/T$, benzoic acid in dry nitrogen. (b) $\ln k$ (Zero-order) vs. $1/T$, benzoic acid in dry air.

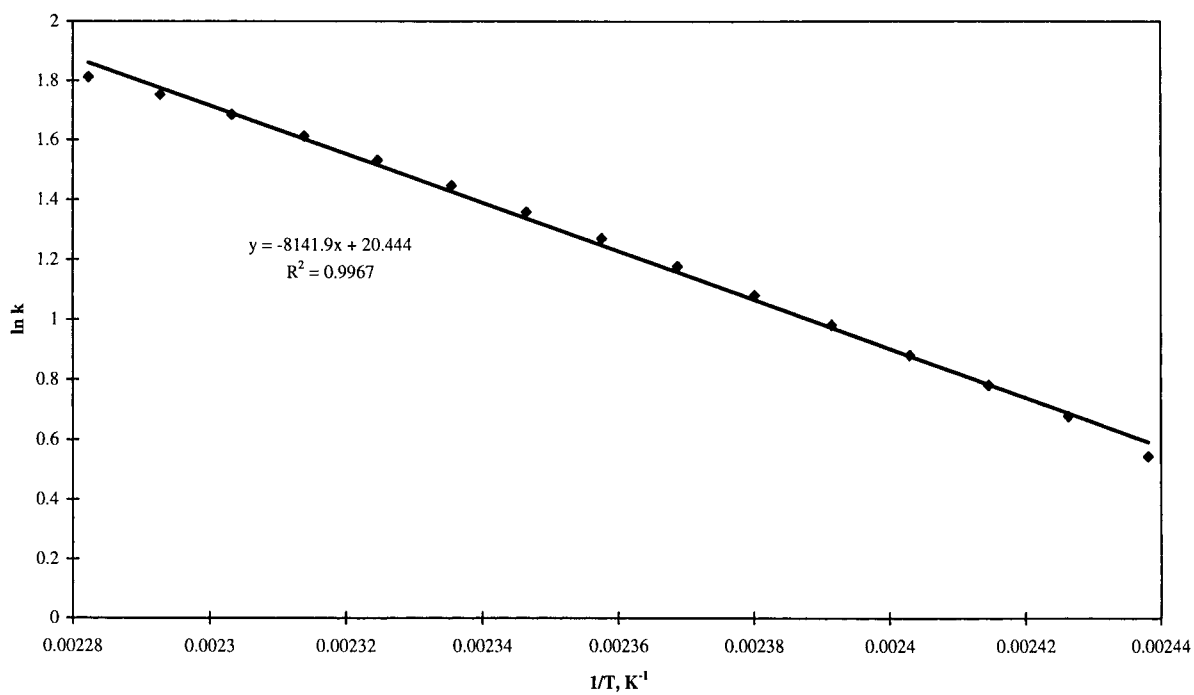
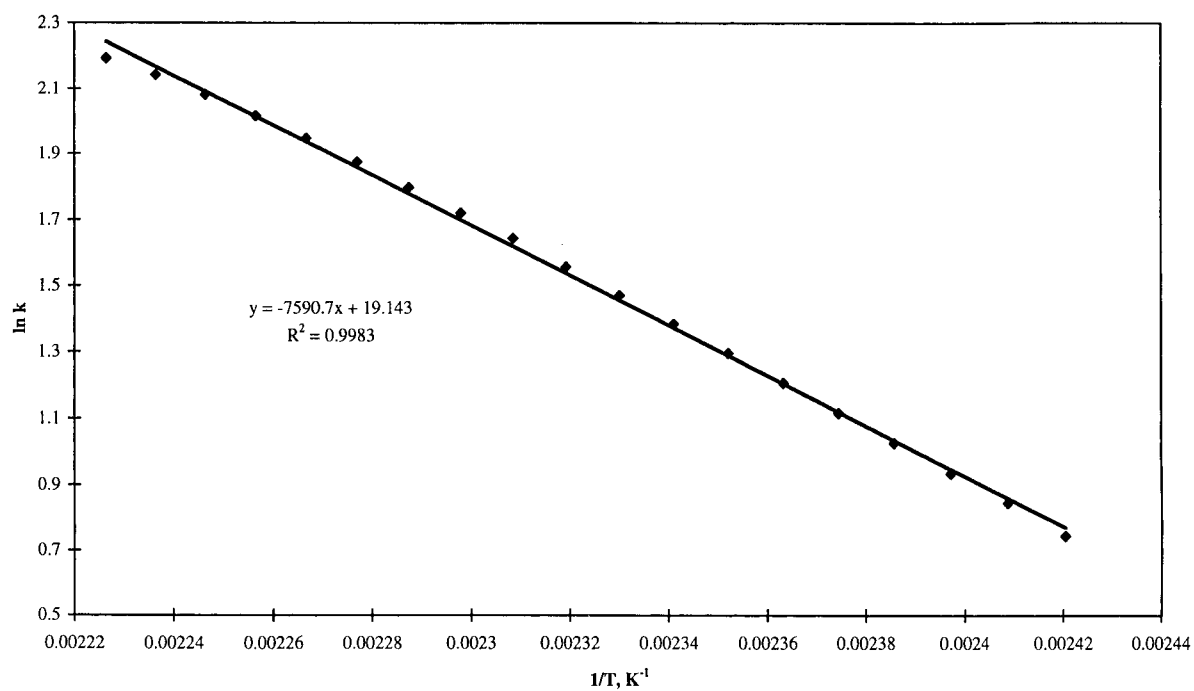


Fig. 8. (a) $\ln k$ (Zero-order) vs. $1/T$, sorbic acid in dry nitrogen. (b) $\ln k$ (Zero-order) vs. $1/T$, sorbic acid in dry air.

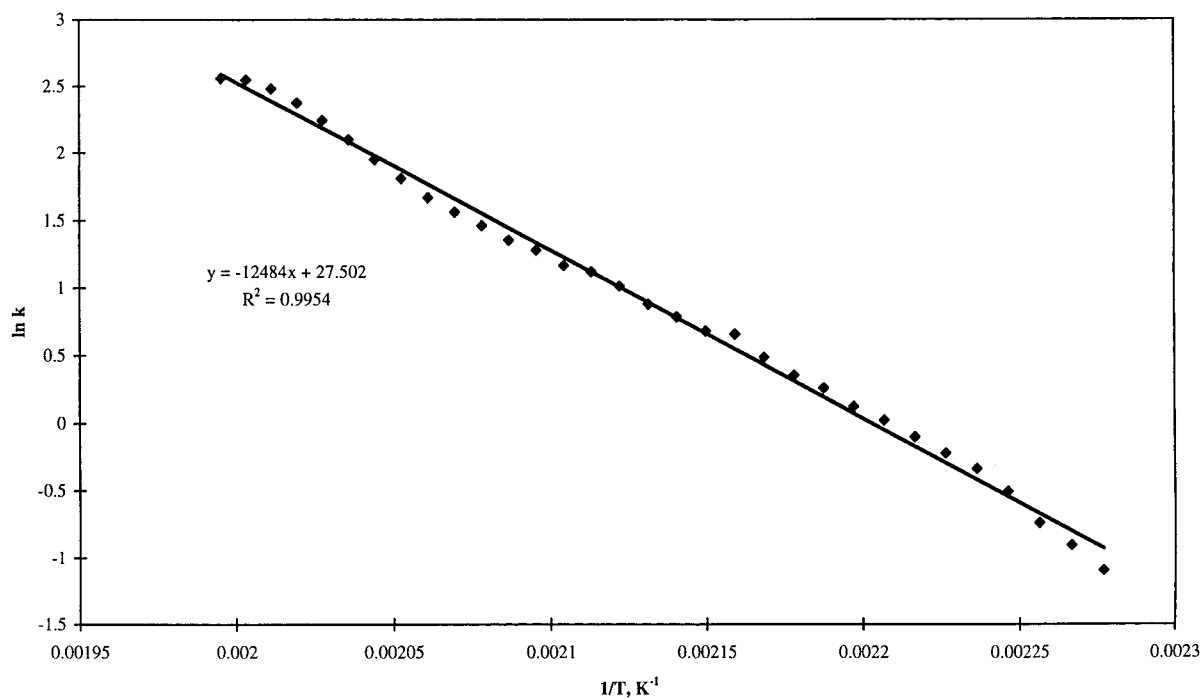
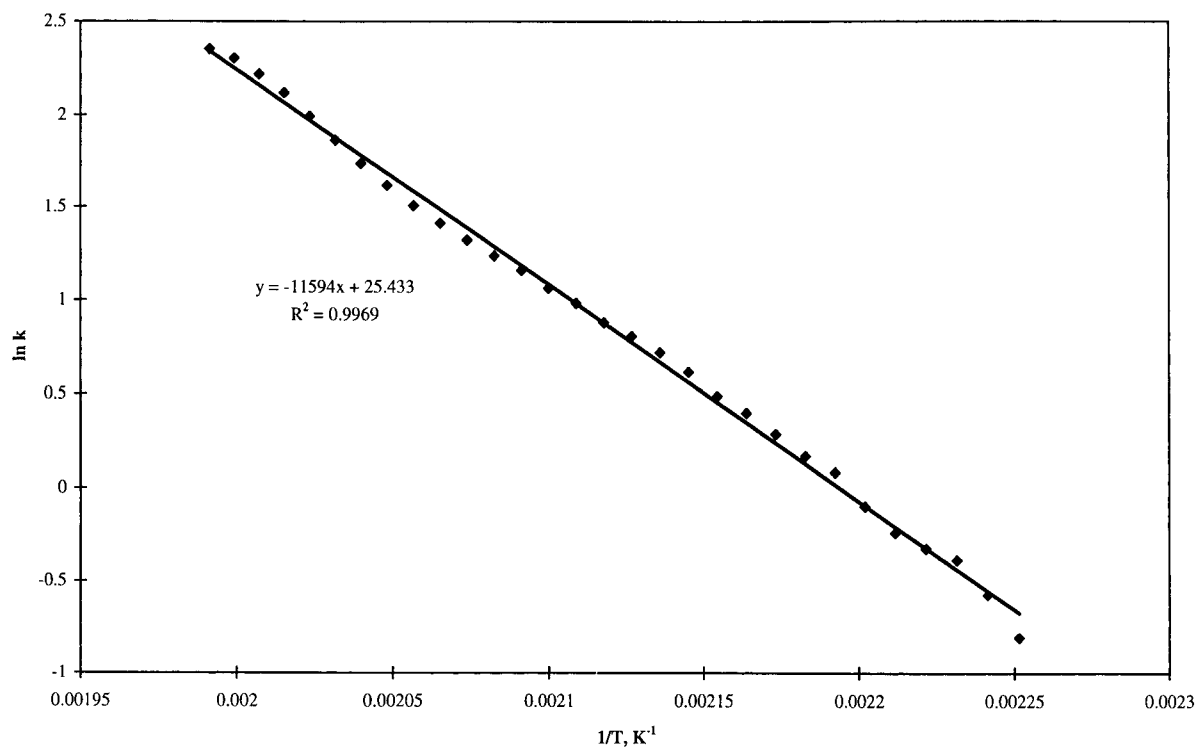


Fig. 9. (a) $\ln k$ (Zero-order) vs. $1/T$, citric acid in dry nitrogen. (b) $\ln k$ (Zero-order) vs. $1/T$, citric acid in dry air.

heated in nitrogen and those heated in air. The effects exerted by the purge gas include the combustion of the residues and the slight inhibition of the evaporation of benzoic acid. Table 4 contains a summary of the Arrhenius parameters of the preservatives.

The activation energy of evaporation can be correlated with the enthalpy of vaporization (H_{vap}). The enthalpy can be calculated using Trouton's rule, as follows

$$\Delta H_{\text{vap}} = T_b \times 88 \text{ KJ K}^{-1} \text{ mol}^{-1} \quad (9)$$

where T_b is the boiling point [12]. For example, the boiling point of benzoic acid is 522.35 K and, using Eq. (9), ΔH_{vap} is 46.22 KJ mol⁻¹. Trouton's rule often fails for associating substances, such as acids [12]. A combination of Trouton's and Hildebrand's rule gives a more accurate value, as shown below:

$$\Delta H_{\text{vap}}/T_b = k'' + R \ln T_b \quad (10)$$

where R is the gas constant and k'' the Kistiakowsky constant (36.61 J K⁻¹ mol⁻¹). Using Eq. (10), ΔH_{vap} is 46.30 KJ mol⁻¹, a much lower value than the activation energy, confirming the failure of Trouton's rule for acids. The results also suggest that benzoic acid exists as a dimer in the solid state.

Barbooti and Al-Sammerrai studied the thermal decomposition of citric acid using, TG, DTG and DSC [13]. They found that the decomposition was effected by the particle size and the heating rate. The decomposition followed the D3 three-dimensional diffusion mechanism. The authors obtained the value of activation energy at 200.2 KJ mol⁻¹. The gas-flow rate was 25 ml min⁻¹, it being much lower than the flow rate used in this study. This confirms the theory that the coefficient of decomposition and the activation energy are dependent on flow rate. It is expected that the activation energy would be lower with high flow rates, because the product is swept away at a much faster rate, favoring the formation of the product.

3.2. Scanning electron microscopy

The untreated sample of citric acid consisted of irregularly shaped solid granules. Some of the particles contained small fissures on the surface of the granules. The samples were magnified 200 \times , as it was difficult to focus at higher magnifications. The heated-treated sample consisted of an irregularly shaped

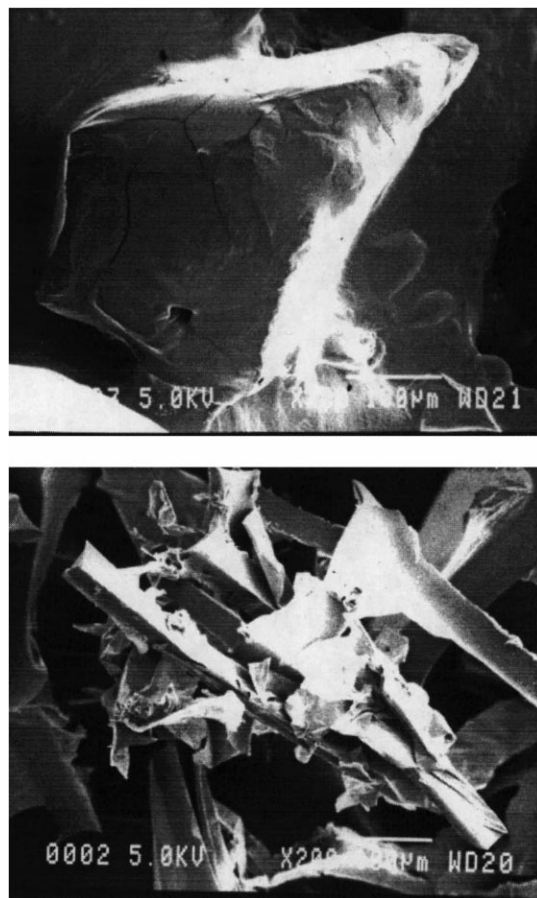


Fig. 10. (a) SEM photograph of untreated citric acid. (b) SEM photograph of heat-treated citric acid.

network of residue, which was hollow in the interior. It appears that the decomposition was initiated in the center of the granules, leaving a framework of brown residue. SEM photographs can be found in Fig. 10.

4. Conclusions

This study indicates that a zero-order process describes the TG plots for benzoic and sorbic acid. A zero-order process best describes the TG plots for citric acid. However, a combination of two or more kinetic mechanisms is occurring, during the decomposition of citric acid. The benzoic acid and sorbic acid would seem to be going through a process of almost complete gasification from a liquid phase. It should be stressed that benzoic acid goes through an

evaporation process from a liquid to a vapor and that no sublimation occurs. This has some bearing on the use of the benzoic acid melting point as a possible temperature and enthalpy standard in thermal analysis. The citric acid also undergoes almost complete gasification, but the thermal analysis data in air shows combustion of a small amount of carbonaceous material at 471°C. The sorbic acid also produced a small amount of a carbonaceous residue. The transition compounds produced by the degradation of sorbic and citric acids are thermally stable relative to the acids, as they decompose at much higher temperatures.

References

- [1] M.E. Brown, D. Dollimore, A.K. Galwey, in: C.H. Bamford, C.F. Tipper (Eds.), *Comprehensive Chemical Kinetics*, Reactions in the Solid State, Vol. 22, Elsevier, Amsterdam, 1980, pp. 1–9; 12–15; 115–117.
- [2] P.J. Haines, *Thermal Methods of Analysis*, Chap. 2, Blackie Academic & Professional, London, 1995.
- [3] D. Dollimore, T.A. Evans, Y.F. Lee, F.W. Wilburn, *Thermochim. Acta* 198 (1992) 249–257.
- [4] M.E. Brown, *Introduction to Thermal Analysis*, Chapman & Hall, London, 1988, pp. 127–134.
- [5] D. Dollimore, P. Tong, K.S. Alexander, *Thermochim. Acta*, 282/283 (1996) 13–27.
- [6] D. Dollimore, T.A. Evans, Y.F. Lee, F.W. Wilburn, *Thermochim. Acta* 188 (1991) 77–85.
- [7] J.P. Murray, K.J. Cavell, J.O. Hill, *Thermochim. Acta* 36 (1980) 97–101.
- [8] M.R. Holdiness, *Thermochim. Acta* 68 (1983) 375–377.
- [9] M. Davies, J.I. Jones, *Trans. Faraday Soc.* 50 (1954) 1042.
- [10] J.H. Kennedy, P.W. Carr, *Thermochim. Acta* 7 (1973) 325.
- [11] H. Briehl, J. Butenuth, *Thermochim. Acta* 167 (1990) 263.
- [12] V. Majer, V. Svoboda, J. Pick, *Heats of Vaporization of Fluids*, Elsevier, Amsterdam, 1989, pp. 164–165.
- [13] M.M. Barbooti, D.A. Al-Sammerrai, *Thermochim. Acta* 98 (1986) 119–126.