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Thermochimica Acta 340–341 (1999) 139–146

thermochimica
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The analysis of perfume fixatives by simultaneous TG–DTA studies

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Accepted 6 August 1999

Abstract

In this study, the coefficient of evaporation values, activation energies and pre-exponential factors were determined for two fixatives, namely benzophenone and cinnamic acid. Simultaneous TG–DTA data and rising temperature kinetics were used for this purpose. The coefficient of evaporation values at different temperatures were determined using rising temperature data obtained from DTG plots. These were then used to calculate the activation energy for the endothermic process of evaporation, on the basis that the rate mechanism is of zero order. The pre-exponential factors were obtained from corresponding kinetic plots. The results show that the activation energy for this evaporation process approaches the enthalpy of vaporization, which is in agreement with the simple relationship between these two for any given endothermic process. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Benzophenone; Cinnamic acid; Fixatives; Evaporation; TG–DTA

1. Introduction

Shampoos, colognes, shower gels and lotions are a few cosmetic preparations that are used frequently in a person's daily cleansing ritual. The ordinary consumer often overlooks the different components that make up these personal care products. However, if one is interested in finding out about the different ways in which each component that is present in a cosmetic preparation behaves in the presence of its co-components, the results of studies that are conducted by thermal analysis techniques may shed some light on this matter.

The rate at which individual components within a cosmetic preparation evaporate is crucial in determining the overall rate of evaporation of the cosmetic formulation. It has been shown that the rate of evaporation for such purposes may be determined from data that is obtained from a simultaneous TG–DTA unit [1]. In this instance, benzophenone and cinnamic acid were studied via thermogravimetry [2]. The knowledge of the rate of evaporation of the various components within a system leads to a multitude of possible applications. With this information on hand, the composition of a cosmetic formulation may then be adjusted to procure a desired shelf life for that cosmetic product in question.

In this study the rate of evaporation of benzophenone, CAS number 119-91-9 and cinnamic acid, CAS number 140-10-3 were examined. Both substances may be classified as fixatives. The role of fixatives is to reduce the proclivity of an odor component to vaporize, thereby making the odor last longer. Benzophenone is an ingredient that is present in everyday

PII: S0040-6031(99)00260-9

home care products. It may be found in shampoos, shower gels, colognes and facial toners. In most of these cosmetic preparations, benzophenone functions as a fixative and controls the rate at which some of the other ingredients present in these cosmetic preparations behave [3]. Benzophenone is also found in sunscreen lotions as it has the ability to aid in filtering UV-rays. Cinnamic acid, a lesser-known fixative is also present in cosmetic preparations. However, it is usually used as a fixative for fragrance formulations. It acts solely as a fixative and has no other significant contribution to the cosmetic preparation. Both fixatives were studied via the use of a simultaneous TG–DTA instrument.

When an evaporation process takes place from a well-defined constant surface area, it would be appropriate to conclude that the rate of evaporation is a zero order reaction [4]. The slope from a plot of mass loss against time (t) or temperature (T) would yield the rate of evaporation of the substance of interest. (refer to Fig. 1 for a typical plot). The coefficient of evaporation, k_{evap} may hence be obtained from dividing the rate of evaporation by the cross-sectional surface area of the sample cell.

Based on the Arrhenius equation, it then follows that a plot of ln k_{evap} vs. inverse temperature, $1/T$ (refer to Fig. 5 for a typical plot) in the following form allows for the determination of the activation energy of evaporation and the corresponding pre-exponential factor [5]:

$$\ln k_{\mathrm{evap}} = \frac{\ln A_{\mathrm{evap}} - E_{\mathrm{act\ evap}}}{RT},$$

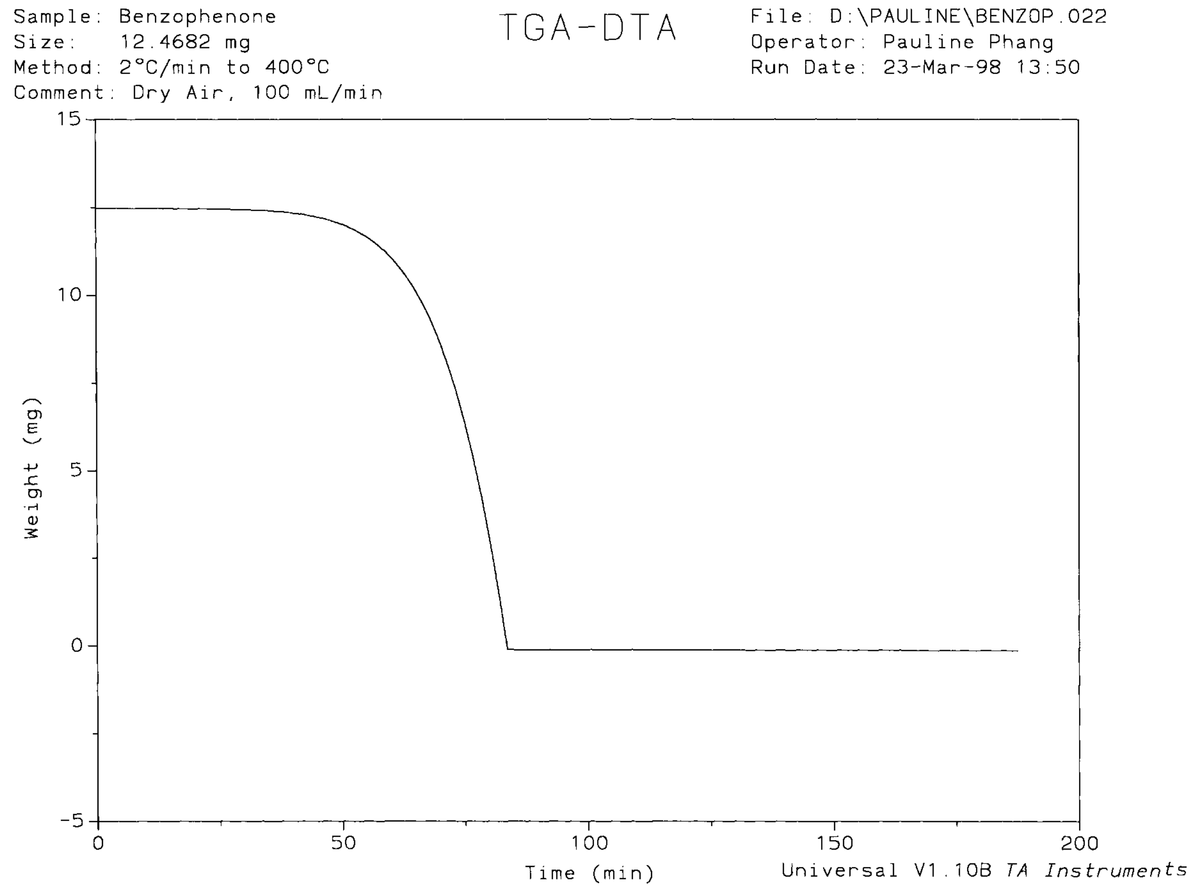

Fig. 1. A typical plot for the evaporation of a fixative, as represented by benzophenone; TG plot of mass loss (in milligrams) against time (in minutes).

where k_{evap} is the coefficient of evaporation at a specified temperature, A_{evap} the corresponding pre-exponential factor, $E_{\mathrm{act\ evap}}$ the energy of activation, T the specific temperature at which the evaporation process takes place and R the gas constant value of 8.3145 J K^{-1} mol^{-1}.

The activation energy of evaporation values for benzophenone and cinnamic acid were also compared with their enthalpy of vaporization values, which were calculated via the Trouton and Hildebrand Rule [6]:

$$\Delta H_{\mathrm{vap}} = T_{\mathrm{b}}(k' + R\ln T_{\mathrm{b}}),$$

where ΔH_{vap} is the heat of vaporization of the substance of interest, T_{b} the temperature of the substance's normal boiling point and k' a constant value of 36.61 J K^{-1} mol^{-1}, determined by Kistiakowsky's Rule [7]. It should be noted that the application of other k' values for the Trouton and Hildebrand Rule have also been suggested [7–9].

In most cases, the activation energy for an entire evaporation process approaches the enthalpy of vaporization in the limit. Fig. 6 is a schematic diagram, which depicts $E_{\mathrm{act\ evap}}$ approaching ΔH_{vap} in the limit. This is in agreement with the basic relationship between these two entities, as is usual for an endothermic process.

2. Materials and methods

The data from thermogravimetry studies of benzophenone were obtained with a simultaneous TG–DTA instrument from TA, model number 2960. The benzophenone and cinnamic acid samples that were used

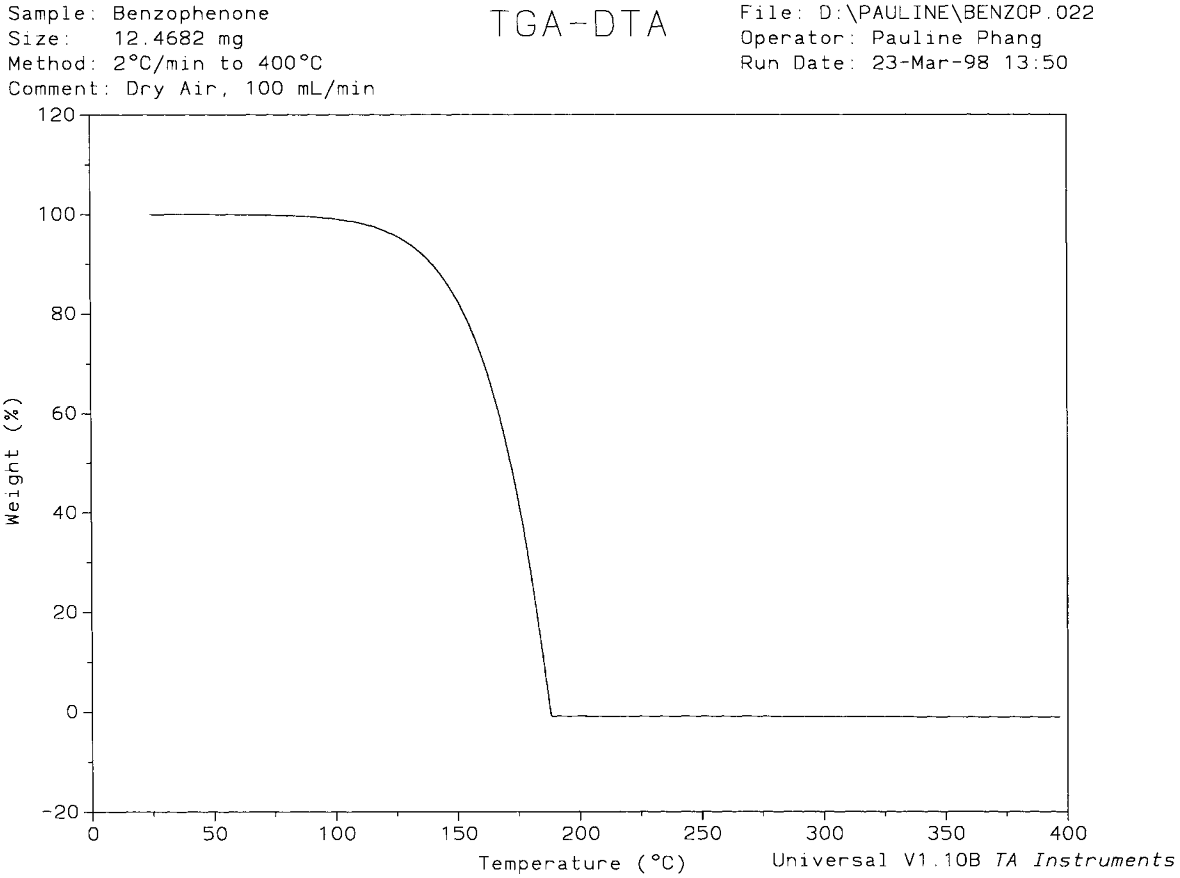

Fig. 2. A typical TG plot of benzophenone depicting percentage mass against temperature for an evaporation process.

for the study were acquired from Aldrich Chemicals. Benzophenone is a white crystalline solid with a geranium-like odor and it has a boiling point of 305°C [10]. Cinnamic acid consists of white crystalline scales and has a boiling point of 300°C [10]. The reference and sample cells used in this study were platinum crucibles. The cross-sectional surface area of the sample cell was determined by calculations based upon multiple diameter measurements of the cell. Both fixative samples were subjected to rising temperature regimes over the range of ambient to a specified final temperature. The two atmospheric conditions under which the samples were investigated include dry breathing air and dry industrial grade nitrogen. The flow rate conditions for the study ranged from 100 to 500 ml min^{-1} in 100 ml increments. The heating rates were also varied and ranged from 2°C min^{-1} to 10°C min^{-1} in 2°C increments.

3. Results and discussion

A typical plot for the evaporation of the fixative of interest is shown in Fig. 1. This is shown as a plot of mass loss (in milligrams) against time (in minutes). In order to calculate the rate of evaporation of the material in mg min^{-1} at each temperature, the area of the sample crucible was determined enabling the rate of evaporation to be calculated in units of mg min^{-1} cm^{-2}. This further allows for the results to be extrapolated to any area of liquid interface. However for the purpose of the evaporation process a plot of percentage mass loss against temperature will suffice. A typical plot of this kind is shown in Fig. 2. All plots for benzophenone and cinnamic acid followed the pattern depicted in these two figures. Similar plots for cinnamic acid were also obtained. To calculate the coefficient of evaporation the

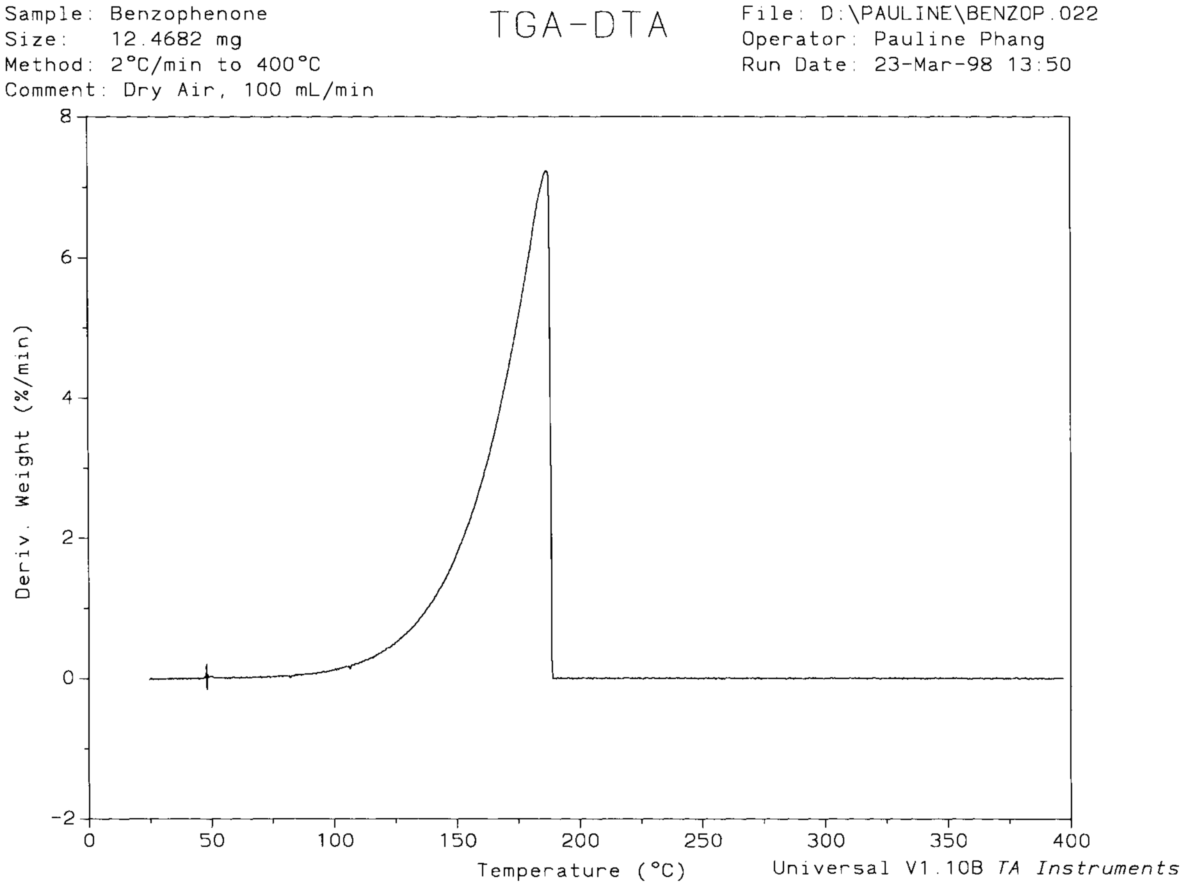

Fig. 3. A typical derivative plot for benzophenone of derivative mass vs. temperature for evaporation processes.

corresponding derivative plots are needed, and an example of one such DTG plot obtained is also shown in Fig. 3.

From the derivative plot shown in Fig. 3 it is noted that the DTG profile observed is characteristic of zero order processes, which would be in accordance with an evaporation process occurring in these experiments. In Fig. 4, the two peaks on the DTA plot provide further evidence that the evaporation process had occurred. The first peak corresponds to the melting point of the fixative. It should be noted that when an experiment is carried out under the conditions of a slow flow rate and a low heating rate, the melting point obtained from the DTA plot is most precise. The melting point values for select experimental conditions are shown in Tables 1 and 2. The second peak, which is indicative of the evaporation process, occurs at a temperature that is below the boiling point of the fixative. This really shows the evaporation process proceeding to completion when all the material has been vaporized. As the quantity of the fixative in the crucible was increased, the temperature at which the second peak materializes approaches the actual boiling point of that particular fixative. The calculation of the activation energy utilized the coefficients of evaporation (as described in Section 1) and a typical Arrhenius plot is shown in Fig. 5. The activation energy of evaporation values and corresponding pre-exponential factors for both fixatives under all conditions studied are given in Tables 3 and 4 (see also Fig. 6).

The enthalpy of vaporization values for both fixatives were also calculated via the Trouton and Hildebrand Rule [6]. This method of calculating the enthalpy

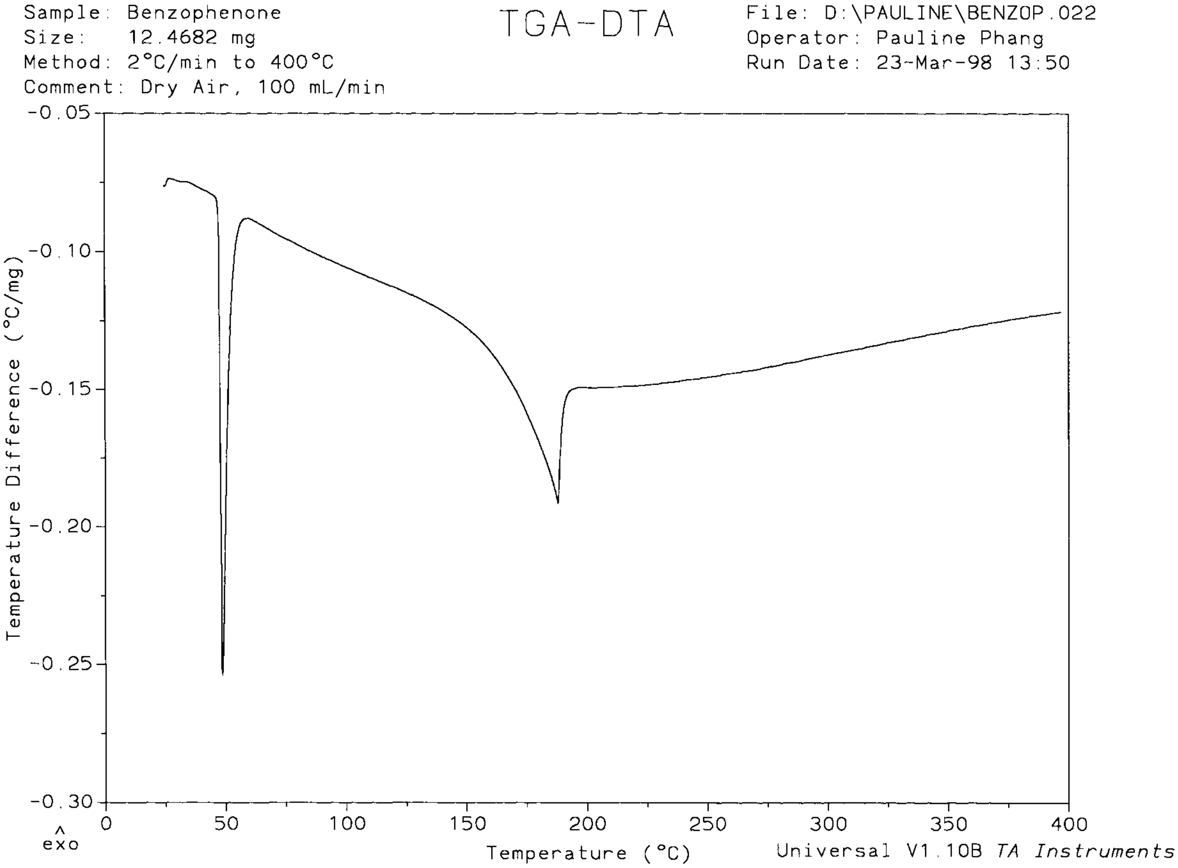

Fig. 4. A typical DTA plot that is obtained for benzophenone, depicting the evaporation process which a fixative undergoes.

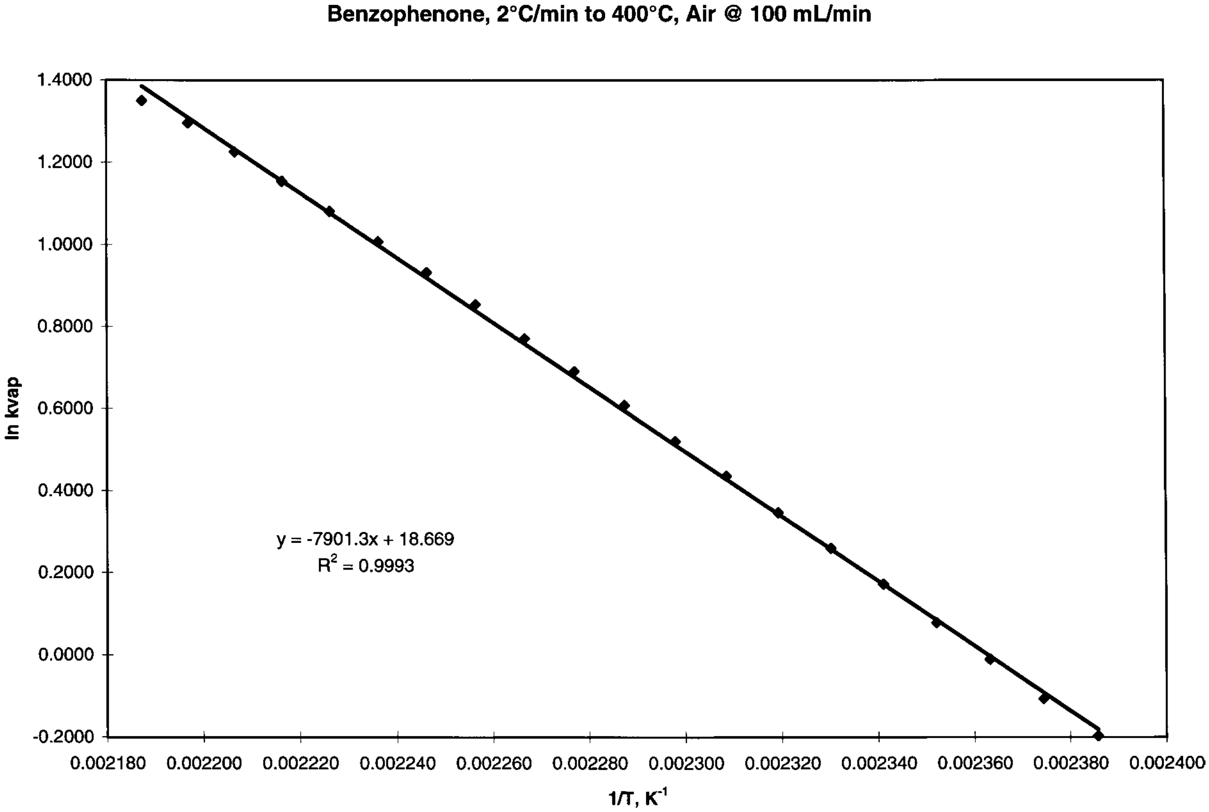

Fig. 5. A typical Arrhenius plot for a benzophenone sample of ln k_{evap} against 1/T.

Table 1
Melting point determination values of benzophenone (select experimental conditions)

Purge gas	Heating rate (°C min^{-1})	Flow rate (ml min^{-1})	Melting point (°C)
Dry air	2	100	48.53
	10	100	51.04
	10	500	51.04
Dry nitrogen	2	100	49.37
	10	100	52.32
	10	500	51.04

Table 2
Melting point determination values of cinnamic acid (select experimental conditions)

Purge gas	Heating rate (°C min^{-1})	Flow rate (ml min^{-1})	Melting point (°C)
Dry air	2	100	133.90
	10	100	136.87
	10	500	135.22
Dry nitrogen	2	100	133.70
	10	100	135.50
	10	500	136.82

of vaporization provides a better approximation, as compared with the result obtained by the application of the basic Trouton Rule. The Trouton and Hildebrand Rule makes the accommodation that the difference between the entropy of the vapor phase and the saturated liquid phase (at a specified standard volume) is assumed to be constant at the normal boiling point [6]. The values determined by these calculations are 51.7 kJ mol^{-1} for benzophenone and 50.4 kJ mol^{-1} for cinnamic acid. These values were lower than all the activation energies that were determined for both fixatives.

Table 3
Activation energies and corresponding pre-exponential factors of benzophenone

Purge gas	Heating rate (°C $\min^{-1}$), flow rate (ml $\min^{-1}$)	E_a (kJ mol^{-1})	ln *A*
Dry air	2, 100	65.7	18.7
	4, 100	60.5	17.4
	6, 100	62.6	17.9
	8, 100	61.1	17.6
	10, 100	58.0	16.8
	10, 200	57.8	16.5
	10, 300	54.5	16.0
	10, 400	55.1	16.2
	10, 500	55.5	16.2
Dry nitrogen	2, 100	68.5	18.9
	4, 100	73.2	20.2
	6, 100	73.0	20.2
	8, 100	72.4	20.1
	10, 100	72.2	20.0
	10, 200	68.8	19.2
	10, 300	65.5	18.4
	10, 400	63.1	17.9
	10, 500	66.9	18.8

Table 4
Activation energies and corresponding pre-exponential factors of cinnamic acid

Purge gas	Heating rate (°C $\min^{-1}$), flow rate (ml $\min^{-1}$)	E_a (kJ mol^{-1})	ln *A*
Dry air	2, 100	68.5	18.9
	4, 100	68.2	19.0
	6, 100	67.0	18.7
	8, 100	69.1	19.2
	10, 100	70.1	19.5
	10, 200	69.2	19.3
	10, 300	64.7	18.3
	10, 400	65.7	18.5
	10, 500	67.2	18.9
Dry nitrogen	2, 100	60.4	17.2
	4, 100	58.6	16.8
	6, 100	57.4	16.6
	8, 100	58.1	16.7
	10, 100	57.3	16.7
	10, 200	55.8	16.3
	10, 300	54.7	16.0
	10, 400	55.6	16.2
	10, 500	56.7	16.5

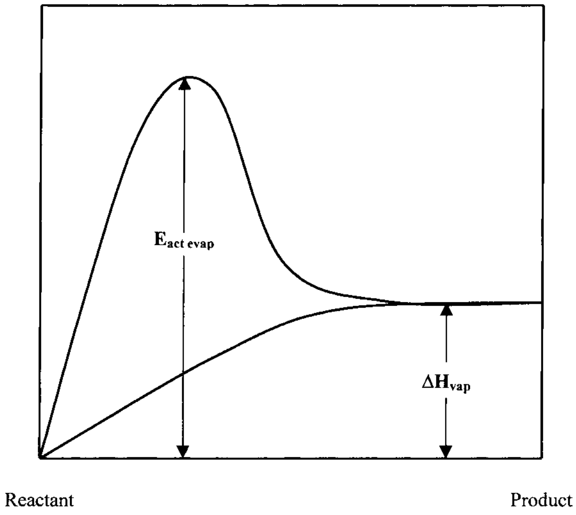

Fig. 6. A schematic diagram depicting $E_{\mathrm{act\ evap}}$ approaching ΔH_{vap} in the limit.

4. Conclusion

From this study, the values of coefficients of evaporation, activation energies and pre-exponential factors were determined for benzophenone and cinnamic acid. Both sets of activation energies (for the various conditions under which the experiments were carried out) were higher than the calculated enthalpy of vaporization values. The melting point determinations from these experiments were precise only when carried out under optimum experimental conditions.

Acknowledgements

The author wishes to thank Dr. Dollimore for his invaluable advice. Dr. Dollimore, many happy returns on your 70th birthday!

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