Jounal of Thermal Analysis, Vol. 49 (1997) 595-599

THE USE OF THERMOGRAVIMETRY TO FOLLOW THE RATE OF EVAPORATION OF AN INGREDIENT USED IN PERFUMES

P. Aggarwal, D. Dollimore and K. Alexander

Department of Chemistry and College of Pharmacy, University of Toledo, Toledo OH 43606, USA

Abstract

Ingredients used in the manufacture of perfumes can be investigated by thermogravimetry. In this study the evaporation of methyl benzoate was investigated using a simultaneous TG-DTA unit. A rising temperature method of thermal analysis was used for the study. The rate of evaporation of the ingredient was calculated from a simple plot of percentage mass loss *vs.* time. A derivative plot of the same was used to calculate the coefficient of evaporation in a controlled atmosphere and regulated air flow rate. In a series of programmed temperature runs on the TG-DTA unit it was shown that the evaporation process is zero order, and that the evaporation coefficients at each temperature can be fitted into the Arrhenius equation. The energy of activation, E_{act} can be calculated from the slope of the line. It was found to be 47 kJ mol^{-1}. This value was compared and shown to approach the enthalpy of vaporization as calculated using the Troutons or Clausius Clapeyron equation

Keywords: methyl benzoate, perfumes, TG

Introduction

Perfumery was once considered to be a creative art. In recent years, the use of sophisticated instrumentation has become vital to the fragrance creator's arsenal. Several analytical tools [1] have become increasingly important in the field of perfumery, such as gas chromatography (GC), GC-MS, ultraviolet spectroscopy and to a lesser extent nuclear magnetic resonance [2]. The use of the GC-MS [3] has clearly been established as a powerful tool to analyze the various components of a fragrance, facilitating a near perfect match or duplication of the fragrance. However there is no analytical tool currently in use to conduct a direct and efficient observation of aging and evaporation studies.

Aging of perfumes can be examined and studied using a thermal [4, 5] balance, in which the sample is heated and the weight changes recorded as the TG signal. The temperature is scanned at a rate of a few degrees per minute while the mass loss is monitored continuously. The thermal curve obtained can provide a quantitative picture of the mass changes occurring in the heated sample being analyzed. Using this method the rates of evaporation of single ingredients present in a perfume

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

are determined and the evaporation rate profile established. An important property that establishes the usefulness of a solvent in a perfume is volatility, that is the propensity of a material to vaporize. The rate of evaporation of an ingredient is governed by volatility. While formulating ingredients for their use in perfumes there has to be a balance between the individual ingredients, one which lifts the fragrance and the other which helps in allowing the fragrance to linger for a while. So the rates of evaporation of individual components in a formulation play an important role in imparting bloom characteristics to a fragrance [6, 7]. In this study, the rate of evaporation of methyl benzoate, CAS registry number [93-58-3] was studied using a rising temperature method of thermal analysis on a TG balance. Methyl benzoate is used as a base in certain perfumes. It is found in essential oils and has a dry fruity, slightly phenolic odor.

Materials and methods

The study was conducted using a thermogravimetry balance from TA instruments simultaneous TG-DTA unit, model # 2960. Uniform platinum pans were used to hold milligram quantities of the material under study. An empty crucible was used as the reference material. The study was carried out using a rising temperature method. The ingredient under study was held in the sample crucible under a constant flow rate of dry air, and the percentage mass loss was examined from the thermal curve. Five different air flow rates 25, 50, 100, 150 and 200 ml min^{-1} were used. The heating rate was also varied. A heating rate of 2, 4, 6, 8, and 10°C min^{-1} was used. The rate of evaporation k, was then calculated from the derivative plot of time *vs.* percentage mass loss. This was repeated at different times on the derivative plot and the activation energy was calculated from an Arrhenius plot of ln k *vs.* temperature. The experiments were repeated three times at each flow rate and each different heating rate employed.

Methyl benzoate was purchased from Aldrich Chemicals and the flow rate was regulated using an electronic flow meter from J & W. Scientific.

Results and discussion

The amount of material lost using different heating rates from a constant surface area was obtained from the TG profile. A typical plot of percentage mass loss *vs.* time constructed using the TG balance is shown in Fig. 1. From this data the coefficient of evaporation was calculated using a derivative (DTG) plot of percentage mass loss *vs.* time as can be seen from Fig. 1. Any point on this plot is proportional to the percentage mass lost per unit area and this will hold while zero order conditions prevail. A typical DTG plot for evaporation of methyl benzoate is thus characteristic of a zero order reaction [8] occurring in a rising temperature mode (Fig. 1). The conditions for zero order break down near the boiling point or when there is little material left. The coefficient of evaporation at any temperature can be read off

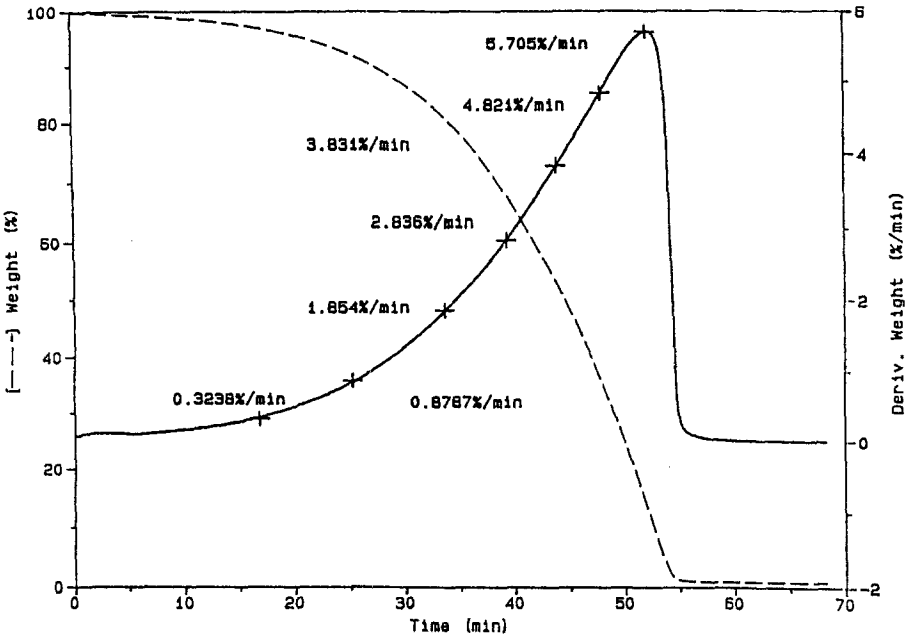

Fig. 1 A typical TG-DTG plot of percentage mass loss *vs.* time for the evaporation of methyl benzoate at 2°C min^{-1} in an atmosphere of flowing dry air with the values for k, the coefficient of evaporation indicated at different temperatures

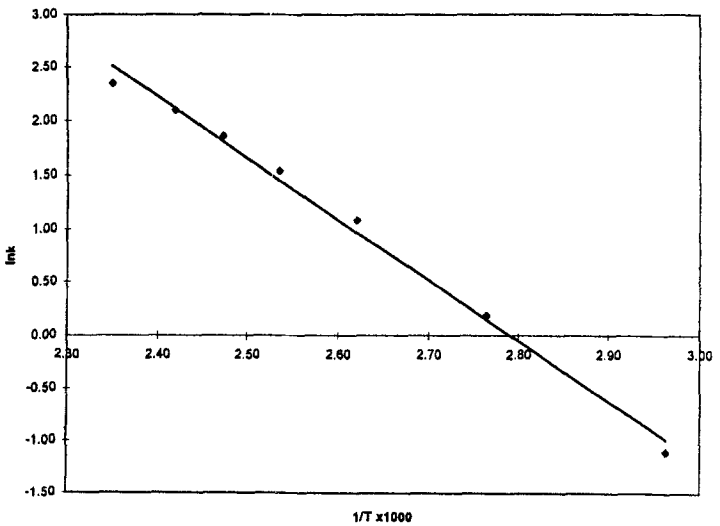

Fig. 2 A typical Arrhenius plot for the calculation of the activation energy E_{act}, for the evaporation of methyl benzoate

from the DTG plot. This value of k is then plotted *vs.* temperature to construct the Arrhenius plot of the form;

$$\ln k(T) = \ln A - E_{act}/RT \quad (1)$$

where k=coefficient of evaporation at temperature T (as read from the DTG plot) A is the Arrhenius parameter and E_{act} the energy of activation.

A typical Arrhenius plot of this kind is shown in Fig. 2 and from this the Arrhenius parameters A and E_{act} can be calculated. The slope obtained at each heating rate gave the value for E_{act}. The intercept corresponds to the A value. An average value for A was found to be 15×10^3. Table 1 gives the values of E_{act} calculated at different flow rates and different heating rates by this method. An average value for E_{act} was found to be equal to 47 kJ mol^{-1}. Using Trouten Rule [9] the enthalpy for vaporization (ΔH_{vap}) was found to be 40.1 kJ mol^{-1}. Clausius Clapeyron [10] gave a value of 53.9 kJ mol^{-1} for the ΔH_{vap} value. Similar values were obtained at different heating rates used, indicating that the results were independent of the heating rate employed over a reasonable extent. This showed that the TG could be used in the rising temperature mode to obtain information on the rates of evaporation of individual ingredients comprising a perfume.

Table 1 Values of activation energy E_{act} calculated at different flow rates and different heating rates from Arrhenius plot

Heating rate/ °C min^{-1}	E_{act}/kJ mol^{-1} at 200 ml min^{-1} flow rate	E_{act}/kJ mol^{-1} at 150 ml min^{-1} flow rate	E_{act}/kJ mol^{-1} at 100 ml min^{-1} flow rate	E_{act}/kJ mol^{-1} at 50 ml min^{-1} flow rate	E_{act}/kJ mol^{-1} at 25 ml min^{-1} flow rate
10	49.00	43.30	48.07	45.00	50.70
8	46.16	43.90	42.30	43.70	53.05
6	47.12	45.50	48.70	43.50	51.40
4	48.40	41.55	50.50	47.40	48.50
2	43.90	47.50	49.70	45.70	47.00

Conclusions

The rates of evaporation of methyl benzoate were calculated from a simple DTG plot and the Arrhenius plot was constructed from that, providing a simple tool for the convenient and easy investigation of perfumery ingredients, making the task reproducible and expedite. This investigation indicated that the TG can be used at different heating rates providing a standard analysis equipment on the basis of which various ingredients in a perfume can be studied.

References

1 R. J. Leibrand and B. D. Quimby, Perfumer and Flavorist, 19 (1994) 25.
2 M. L. Hagedorne, J. Agr. Food Chem, 40 (1992) 634.

3 D. Walker, K. D. Bartle, D. Breen, A. A. Clifford and S. Costious, Analyst, 119 (1994) 2789.
4 M. Brown, Introduction to thermal analysis, 2nd ed., Chapman and Hall, London 1988, p. 50.
5 C. J. Keattch and D. Dollimore, An Introduction to thermogravimetry, 2nd ed.; Heyden, London 1975, p. 164.
6 R. R. Calkin and J. Stephan, Perfumery Practice and Principles, John Wiley and Sons, Inc., New York 1994, p. 277. .
7 K. Bauer, D. Garbe and H. Surburg, Common Fragrance and Flavor Materials, 2nd ed.; VCH publishers, New York 1990, p. 218.
8 D. Dollimore, T. A. Evans, Y. F. Lee and F. W. Wilburn, Thermochim. Acta, 198 (1992) 249.
9 R. M. Stephenson and S. Malanowski, Handbook of the Thermodynamics of Organic Compounds, Elsevier Science publishing Co. Inc., New York 1987, p. 552.
10 V. Majer, V. Svoboda and J. Pick, Heats of Vaporization of fluids, Elsevier, New York 1989, p. 344.