

KINETICS OF MALEIC ANHYDRIDE VAPORISATION

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(Received 3 July 1989)

ABSTRACT

The rates of maleic anhydride vaporisation have been measured at temperatures between 263 and 360 K in flowing argon at atmospheric pressure using a recording electrobalance. Measured rates spanning over four orders of magnitude agree well with the transition state theory for first-order desorption.

INTRODUCTION

Maleic anhydride reacts with dienes to form adducts. These Diels–Alder reactions can be used to eliminate unwanted dienes from hydrocarbon mixtures and, for analytical purposes, in gas chromatography [1]. As maleic anhydride sublimates or evaporates quite readily, the kinetics of maleic anhydride vaporisation play an important role in these processes. We undertook the measurements described in this paper after a computer search of the Chemical Abstract databases over the past 22 years failed to reveal any sublimation or evaporation rate data for maleic anhydride.

EXPERIMENTAL

Maleic anhydride, 99% pure, was further purified by sublimation under vacuum at 305 K and condensation at 290 K. Melting temperatures for the anhydride before and after purification were determined using a DuPont differential scanning calorimeter. A phase transition peak was observed at 323.5 K when heating the purified sample at a rate of 600 K h⁻¹. This value agrees well with the melting point for maleic anhydride given in tables as 326 K [2].

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The purified anhydride was melted and poured onto a flat Pyrex glass surface. Slabs approximately $1 \times 1 \times 0.15$ cm in size were cut with a blade, tied with a 3-cm length of 0.012-mm diameter tungsten wire and hung from one arm of a Cahn-2000 recording electrobalance interfaced with an IBM-XT computer. The sample hung in the centre of a Pyrex glass tube (20 mm internal diameter) fitted with a heat exchange jacket. Argon gas, purified by passage through a molecular sieve bed, flowed downwards in the glass tube with a superficial velocity u_s of 64 cm s^{-1} . A series of test runs showed that the evaporation rate for maleic anhydride in our experimental set-up was independent of the carrier gas velocity for $u_s > 32 \text{ cm s}^{-1}$. An antifreeze solution was kept at constant temperature by a cryostat/thermostat controller and circulated through the heat exchange jacket. A type K thermocouple was placed next to the sample and connected to a cold (273 K) reference junction. A 6-digit DVM was used to read temperatures. Temperatures were kept constant to better than $\pm 0.2 \text{ K}$ during the runs.

A separate series of runs was carried out with the 0.95-cm diameter aluminium bucket of the recording electrobalance filled with maleic anhydride chips and heated to melting temperature. Both evaporation and sublimation rates were measured on these samples.

In a typical run, the sample weight was continuously monitored on the computer screen. After the desired temperature was reached, it was kept constant for about 500 s. The sample weight was then recorded at time intervals of 2 s. At least 200 data points were recorded before resetting the temperature for another run. Linear regression of the weight versus time data resulted in straight lines with individual data points deviating from the regression value by less than 10%. The slopes of those straight lines were taken as the rates of vaporisation of the sample. Dividing those rates by the geometrical surface area of the samples yielded the specific vaporisation rates.

RESULTS AND DISCUSSION

An Arrhenius plot showing specific vaporisation rates versus reciprocal temperature is shown in Fig. 1. Although the true surface area of our samples is not known, the fact that rates measured on samples with different geometry (slab and bucket) fell on the same straight lines suggests that the geometrical area is a reproducible measure of the true surface area. Linear regression analysis of these data yields, for $T < 325 \text{ K}$, the specific rate of sublimation in milligrams of maleic anhydride evaporated per square centimetre of a sample per second, v_s

$$\ln v_s = 24.87 - 9788/T \quad (1)$$

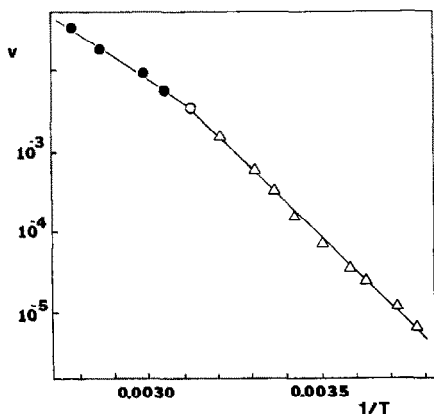


Fig. 1. Rates of maleic anhydride evaporation, expressed in $\text{mg cm}^{-2} \text{s}^{-1}$ (filled symbols), and rates of maleic anhydride sublimation (open symbols) vs. $1/T$ (K^{-1}). Circles denote rates measured on samples contained in the aluminium bucket of the recording electrobalance. Triangles indicate rates measured on samples in the form of slabs. The solid lines are calculated from eqns. (1) and (2).

For $T > 325$ K, the specific rate of evaporation v_e is obtained from

$$\ln v_e = 14.68 - 6519/T \quad (2)$$

The variance of the regression analysis is 8.99×10^{-3} and 4.46×10^{-3} , respectively. The straight lines intercept at $T = 321$ K, within 2 K of the melting point of our samples. The slopes of the Arrhenius plot straight lines yielded the activation energies for sublimation, $E_s = 81.41 \text{ kJ mol}^{-1}$, and for evaporation, $E_e = 54.22 \text{ kJ mol}^{-1}$.

According to transition state theory [3], the rate of desorption v for a first-order process is

$$v = (kT/h) \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)n \quad (3)$$

Assuming the surface concentration of solid maleic anhydride to be $n = 9 \times 10^{14} \text{ molecules cm}^{-2}$, the pre-exponential term for first-order desorption is $A_s = 4.3 \times 10^{14} \text{ s}^{-1}$. As $kT/h \approx 10^{13} \text{ s}^{-1}$, from the experimental value for A_s we obtain $\Delta S^\ddagger \approx 30 \text{ J mol}^{-1}$. This value is about one third of the entropy of sublimation and it indicates that a maleic anhydride molecule gains some degrees of freedom as it reaches the transition state. The enthalpy of formation of the activated complex ΔH^\ddagger corresponds to the measured activation energy E_s . As the heat of vaporisation for maleic anhydride is about 50 kJ mol^{-1} and the heat of fusion is 13 kJ mol^{-1} , we conclude that the kinetic activation barrier for sublimation is about 18 kJ mol^{-1} . This value should indicate that sublimation occurs in a series of steps.

The rate of evaporation of a liquid is given by the transition state theory [4] as

$$v = \alpha P(2\pi MRT)^{-1/2} \quad (4)$$

where P is the vapour pressure in equilibrium with the liquid and α is the ratio of rotation partition functions for surface molecules to those in the vapour phase. Calculations of α comparing entropies of vaporisation of maleic anhydride and carbon tetrachloride at equal vapour to liquid volume ratios [4] result in values for α within the same order of magnitude as those observed experimentally ($\alpha \approx 6 \times 10^{-5}$). This low value indicates that rotation of the molecules on the surface of the liquid is restricted.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Héctor Asencio, who built the glass system, and to Ms. Diana Fasce, who operated the differential scanning calorimeter.

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