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CONTROLLED-RATE THERMAL DESORPTION

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Abstract

A new way of conducting thermal desorption experiments is described. The method consists in maintaining the desorption rate constant by a rigorous control of temperature. The equations for two models of constant rate desorption are described: from a surface with only one type of adsorption site, and with two different types.

The technique is applied to two real systems and the kinetic parameters are determined. The results are compared with those obtained by using TPD. The main advantages are discussed and the methodology and modifications required for a TPD set-up to work at a constant desorption rate are described.

Keywords: controlled rate thermal analysis, thermal desorption, TPD

Introduction

Temperature-programmed desorption (TPD) is a technique in which a solid with an adsorbed substance is heated in accordance with a preset program. With the increase in temperature, the adsorbed molecules are desorbed and carried by an inert gas to a detector, where a physical property related to the concentration of the desorbed species is measured. Thus, the detector signal is a direct measurement of the desorption rate. During the experiment, the desorption rate is recorded against temperature (TPD curve). The amount of substance desorbed is given by the area of the TPD curve.

The rate equation describing TPD correlates three variables: the desorption rate, $v=-dN/dt$; the amount of substance adsorbed, N; and temperature, T. Time and temperature are related by the heating rate, $\beta=dT/dt$.

Some years ago, several researchers proposed another way of carrying out experiments on thermal analysis [1–6]. This new procedure does not involve a preset heating program, but rather the sample is heated in such a way that it is possible to keep the rate of the process constant. It is now the value of the detector signal which controls the sample heating. Under these conditions, there is no point in plotting velocity against temperature and the information on the process is ob-

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tained from the recording of the heating curve, *t vs. T*. Since the experiment proceeds at a constant rate, the equation describing the process is simpler since it involves only two variables; *t* and *T*.

In the present work, we have applied this new method of carrying out thermal analysis experiments to the particular case of TPD. Following the recommendations of the International Committee of Thermal Analysis [7], we have called this technique controlled-rate thermal desorption (CRTD). Firstly, we develop the equations describing the process and those that permit the estimation of the kinetic parameters for two models of desorption: i) simple desorption from a single adsorption site, and ii) simple desorption from a surface with several adsorption sites. We also describe the methodology and apparatus required to carry out the experiments and report the results obtained with two real systems, comparing these results with those obtained with TPD.

Theoretical development

Simple desorption from a single adsorption site

For a process of simple desorption of order *n*, the rate equation may be expressed as

$$v = -\frac{dN}{dt} = kN^n = AN^n \exp(-E/RT) \tag{1}$$

where *N* represents the number of moles adsorbed, *k* is the rate constant, *t* is time, *T* is temperature, and *A* and *E* are the activation parameters, i.e. the pre-exponential factor and activation energy, respectively.

Since adsorption takes place at a preset temperature (TPD) with a heating rate of $\beta = dT/dt$, the above equation may be written as

$$v = -\frac{dN}{dt}\beta = AN^n \exp(-E/RT) \tag{2}$$

By contrast, if desorption is considered to take place at constant rate, *C*, the equation describing the rate of the process would be

$$v = -\frac{dN}{dt} = C = AN^n \exp(-E/RT) \tag{3}$$

Bearing in mind that in a CRTD process the rate is constant at all times, the number of moles adsorbed will be

$$N = N_0 - Ct \tag{4}$$

where N_0 is the number of moles adsorbed initially. On combining Eqs (3) and (4), one obtains

$$t = \frac{N_0}{C} - \left(\frac{1}{C^{n-1}A}\right)^{1/n} \exp(-E/nRT) \quad (5)$$

Equation (5) is the equation of a CRTD process. It includes the variation in temperature of the sample with time (heating curve) for the desorption rate to be kept constant.

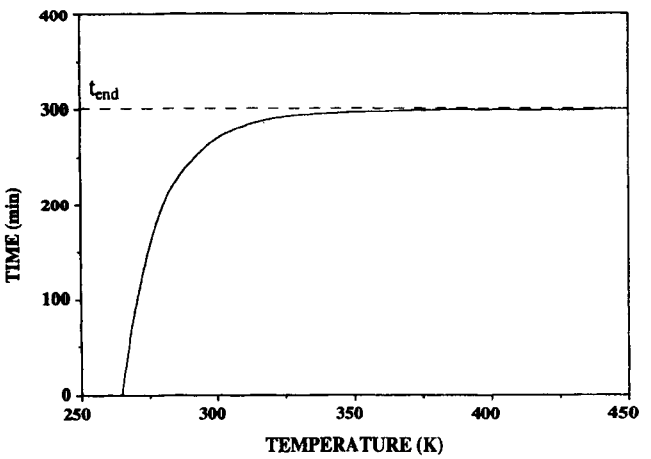

Fig. 1 Simulation of a CRTD experiment from one active site. A=6·10^{-5} min^{-1}; E=41.7 kJ mol^{-1}; T_0=282 K, C=3.33·10^{-8} mol min^{-1}; N_o=1.0·10^{-5} mol

Figure 1 shows the shape of the heating curve for a simulated CRTD experiment for a rate of 3.33 10^{-8} mol min^{-1}. The time required for desorption to be complete is a key point in the heating curve, which we shall call t_{end}. This value is readily calculated via Eq. (4), $t_{end}=N_0/C$, or determined graphically from the heating curve by tracing its horizontal asymptote.

By introducing t_{end} into Eq. (5) and taking napierian logarithms, one obtains

$$\ln(t_{end}-t) = -\frac{1}{n}\ln(C^{n-1}A) + \frac{E}{nR}\frac{1}{T} \quad (6)$$

For the particular case of $n=1$:

$$\ln(t_{end}-t) = -\ln A + \frac{E}{R}\frac{1}{T} \quad (7)$$

The plot of $\ln(t_{end}-t)$ *vs.* $1/T$ is a straight line that allows one to determine E and A in a single experiment. Figure 2 shows this plot for the simulated experiment described in Fig. 1.

Another of the advantages of this procedure is that it allows determination of the kinetic order of the desorption process from two CRTD experiments at differ-

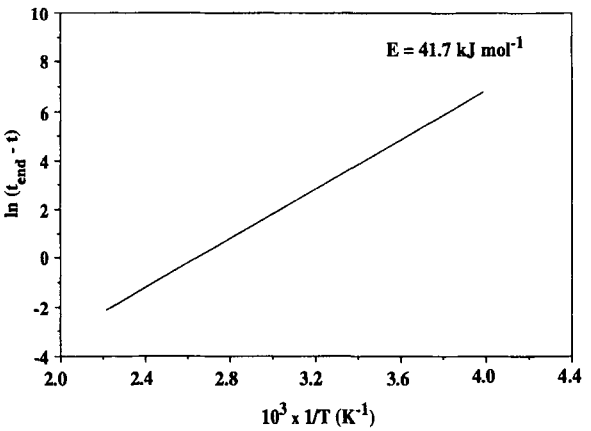

Fig. 2 Determination of the activation energy of desorption for the CRTD experiment simulated in Fig. 1

ent desorption rates, C. According to Eq. (7) (n=1), two experiments carried out at different desorption rates, C, will give the same line on plotting $\ln(t_{end}-t)$ *vs.* $1/T$ and the values of the slope and intercept will remain unaffected. By contrast, if n is different from 1, according to Eq. (6), the value of C will affect the value of the intercept of the plot $\ln(t_{end}-t)$ *vs.* $1/T$ and will not effect the slope value. Accordingly, one will obtain parallel straight lines for different values of C. The value of n is readily determined from the ordinates at the origin O_1 and O_2 of this plot for two experiments with rates of C_1 and C_2:

$$\frac{n}{1-n} = \frac{\ln C_1 - \ln C_2}{O_1 - O_2} \tag{8}$$

Sample desorption from a surface with several adsorption sites

If one considers a simple desorption process from a surface with two adsorption sites, it is possible to express the desorption rates from each of the sites as

$$v_1 = -\frac{dN_1}{dt} = k_1 N_1^n = A_1 N_1^n \exp\left(-\frac{E_1}{RT}\right) \tag{9}$$

$$v_2 = -\frac{dN_2}{dt} = k_2 N_2^n = A_2 N_2^n \exp\left(-\frac{E_2}{RT}\right) \tag{10}$$

where N_1 and N_2 are the numbers of moles adsorbed on sites 1 and 2, respectively; and k_1 and k_2 are the desorption rate constants from sites 1 and 2, respectively.

The desorption rates v_1 and v_2 from each of the adsorption sites are not constant over time, although the sum of the two of them is constant:

$$v = v_1 + v_2 = C = k_1 N_1^n = k_2 N_2^n \tag{11}$$

At the beginning of the experiment, the temperature is low, and desorption from the site with the lowest energy will be the one that contributes most to the overall rate. However, at the end of the experiment, when the temperature is high, desorption will mainly take place from the site with the greatest energy.

If one considers n=1, Eqs (9) and (10) become

$$N_1 = N_{01}e^{-I_1} \quad \text{where} \quad I_1 = \int_0^t A\exp\left(-\frac{E_1}{RT}\right)dt \tag{12}$$

$$N_2 = N_{02}e^{-I_2} \quad \text{where} \quad I_2 = \int_0^t A\exp\left(-\frac{E_2}{RT}\right)dt \tag{13}$$

On substitution in Eq. (11), one is left with

$$C = A_1\exp\left(-\frac{E_1}{RT}\right)N_{01}\exp(-I_1) + A_2\exp\left(-\frac{E_2}{RT}\right)N_{02}\exp(-I_2) \tag{14}$$

which relates T and t, the heating curve when the rate of the overall process v=v_1+v_2 is constant.

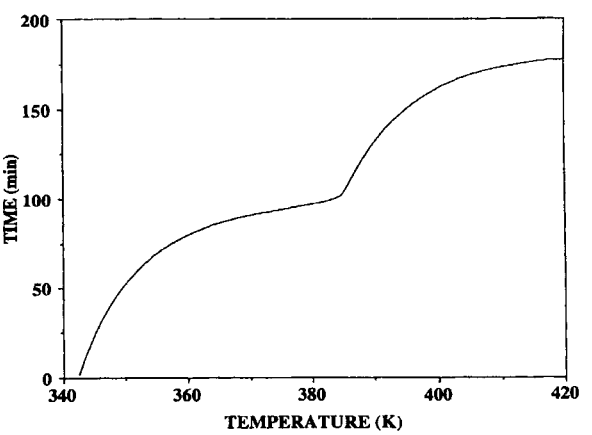

Fig. 3 Simulation of a CRTD experiment from two active sites. A_1=1·10^{14} min^{-1}; A_2=1·10^{14} min^{-1}; E_1=104.17 kJ mol^{-1}; E_2=116.67 kJ mol^{-1}; T_0=342.35 K, C=1.11·10^{-7} mol min^{-1}; N_{01}=1.0·10^{-5} mol; N_{02}=1.0·10^{-5} mol

Figure 3 shows the heating curve of a simulated CRTD experiment in which two adsorption sites with different activation energies of desorption overlap. The values of the integrals I_1 and I_2 necessary for the simulation to be run were calcu-

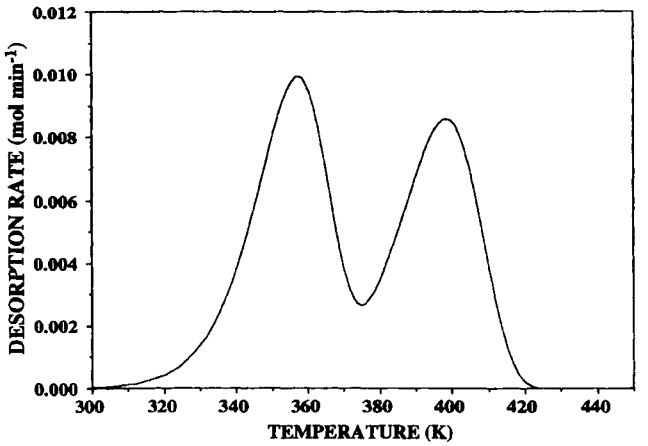

Fig. 4 TPD simulation curve from two active sites. $A_1=1\cdot10^{14}$ min^{-1}; $A_2=1\cdot10^{14}$ min^{-1}; $E_1=104.17$ kJ mol^{-1}; $E_2=116.67$ kJ mol^{-1}; $\beta=0.5$°C min^{-1}; $N_{01}=1.0\cdot10^{-5}$ mol; $N_{02}=1.0\cdot10^{-5}$ mol

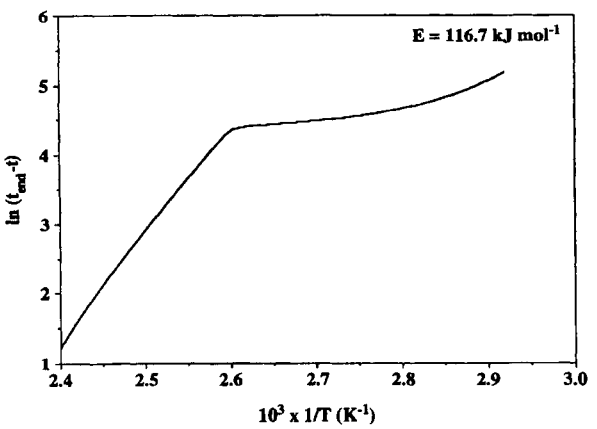

Fig. 5 Determination of the activation energy of the more energetic site for the CRTD experiment simulated in Fig. 3

lated by an approximation method (trapezoidal rule). In the curve, the presence of both types of adsorption site is very clear from the step in the plot. For comparative purposes, Fig. 4 shows the TPD curve for the same system under identical simulation conditions. It has two maxima, corresponding to desorption from the two sites.

Owing to the complexity of Eq. (14), the treatment of the experimental data to obtain the kinetic parameters becomes very complicated. However, it is possible to obtain these parameters with fairly good precision by assuming that at the end

of the desorption experiment the desorbed molecules will come only from the site with the highest energy, such that the plot of $\ln(t_{end}-t)$ *vs.* $1/T$ for the final part of the experiment should be a straight line. Figure 5 shows this plot of the experiment simulated in Fig. 3; perfect linearity is seen at the end of the experiment. The slope and the ordinate at the origin furnish the values of the activation energy, E_2, and the pre-exponential factor, A_2.

Experimental

All experiments were carried out in the liquid phase [8, 9] on a TPD apparatus slightly modified to allow work at a controlled desorption rate. The scheme of the set-up for working conventionally (TPD) and at controlled rate (CRTD) is shown in Fig. 6.

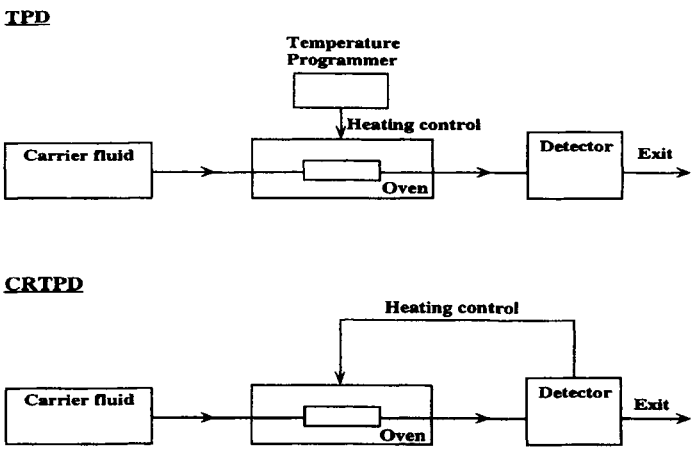

Fig. 6 Scheme of apparatus for thermal desorption working in the TPD or CRTD modes

In the TPD mode, the temperature programmer is responsible for generating a heat ramp in the oven that is linear over time. In the CRTD mode, the programmer is removed and it is the detector that controls the heating in the oven in such a way that the detector signal will always be the same (constant desorption rate). The experimental method is as follows: the sample with the substance to be desorbed is placed in the desorption chamber located inside the oven. The pump that impels the carrier liquid at a constant flow rate is turned on. At the exit of the oven, the stream with the desorbed substance is cooled and thermostated before its arrival at the detector. If the desorption rate (detector signal) is lower than the rate chosen for the experiment, the temperature of the oven is increased automatically so that the desorption rate will increase. In this way, the desorption is made to take place at a constant rate.

The detector employed in the present study was a UV-VIS spectrophotometer (Shimadzu UV-240) with a flow cell with 1 cm optical pathway. The carrier liquid was distilled degassed water. In all the CRTD experiments, the error in the constancy of the rate (the stability in the detector signal) was less than 1%.

The systems chosen to assay the models described were crystal violet adsorbed onto silica gel and C.I. direct green 26 adsorbed onto mercerized cotton. The silica gel was from Merck 60 for chromatography: macroporous with a particle size between 0.2 and 0.5 mm. Its surface area, determined by the BET method from the adsorption-desorption isotherm of N_2 at 77 K, was 316 $m^2 g^{-1}$.

The samples of silica gel employed in this study were prepared by placing a weighed amount of adsorbent in a flask with a known concentration of dye. The amount of dye retained by the silica gel was determined by periodic spectrophotometric control of the solution. After the desired degree of saturation had been reached, the silica gel was removed from the solution, washed several times with distilled water and dried in an oven at 50°C for 2 h. The degrees of saturation of the silica gel employed here were $1.25 \cdot 10^{-6}$ and $3.6 \cdot 10^{-6}$ mol g^{-1}.

C.I. Direct green 26 is a direct dye supplied by Ciba Geigy; it is very well adsorbed onto cotton. The dyeing was performed in a 'Tin-control' laboratory apparatus that simulates the dyeing procedure used on an industrial scale. 5.0 g of mercerized cotton was placed in contact with 200 cm^3 of a solution containing 0.02 g of C.I. direct green 26 dye, 0.02 g of Albatex PON (humectant) and 1.0 g of sodium sulphate (to neutralize the negative electric charge of the fibre and to favour adsorption of the anionic dye). The bath was kept under conditions of shaking for 45 min at a temperature of 98°C. Following this, the material was washed several times with water at 40°C and then in cold water. The degree of saturation employed was $1.01 \cdot 10^{-5}$ mol g^{-1}.

Results

Simple desorption from a single adsorption site

Following this model, two constant rate desorption experiments were carried out, using crystal violet adsorbed into silica gel.

Very low degrees of saturation ($1.3 \cdot 10^{-6}$ and $3.6 \cdot 10^{-6}$ mol g^{-1}) were used in order to avoid surface heterogeneity as far as possible, and so that the experimental conditions would be as close as possible to simple desorption. The desorption rates chosen were $2.05 \cdot 10^{-9}$ and $1.42 \cdot 10^{-9}$ mol min^{-1}, sufficiently low to avoid possible diffusion control. The sample size was 0.0500 g and the flow rate of the carrier water was 8.0 and 7.0 cm^3 min^{-1}, respectively.

Figure 7 shows the temperature *vs.* time dependence required to maintain the adsorption rate constant in both experiments. According to Eq. (6), the plot of $\ln(t_{end}-t)$ *vs.* $1/T$ should be a straight line. The time, t_{end}, necessary to obtain this

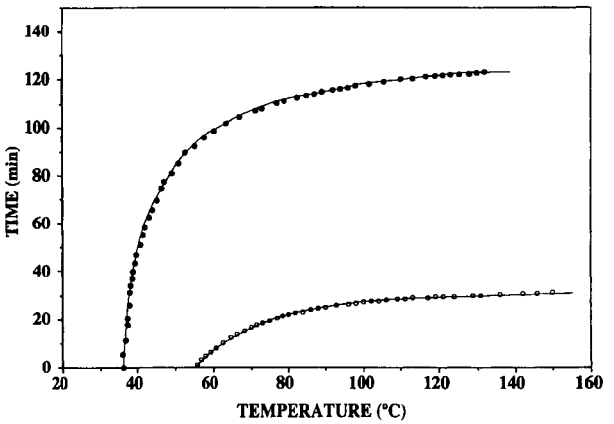

Fig. 7 CRTD heating curve of crystal violet from silica gel.
a) N_0=6.30·10^{-8} mol; F=8.0 cm^3 min^{-1}; C=2.05·10^{-9} mol min^{-1}; w=0.0502 g
b) N_0=1.72·10^{-7} mol; F=7.0 cm^3 min^{-1}; C=1.42·10^{-9} mol min^{-1}; w=0.0500 g

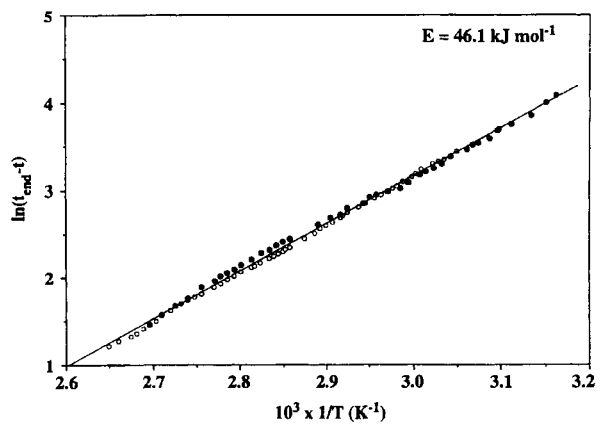

Fig. 8 Determination to the activation energy of desorption of crystal violet from silica gel by CRTD. Observation of first order of desorption

plot was calculated from the desorption rate and from the exact amount of dye collected throughout the experiment. Figure 8 shows these plots for the two rates chosen.

The coincidence of the plots for the two experiments confirms a kinetic order of 1, in agreement with the model. The activation energy determined from the slope was 46.1 kJ mol^{-1}.

This activation energy was compared with that obtained in a TPD study. The most usual method in TPD for obtaining the activation energy of desorption was proposed by Cvetanovic and Amenomiya [10, 11] and is based on the variation in

the position of the maximum of the TPD curves on variation of the heating rate. According to this method, the following relationship between the heating rate, β, and the temperature at which the maximum of the TPD curves appears, T_M, was considered:

$$\ln\frac{\beta}{T_M^2} = \ln\left(\frac{A_d R}{E_d}\right) - \frac{E_d}{R}\frac{1}{T_M} \tag{15}$$

Thus, a plot of $\ln(\beta/T_M^2)$ *vs.* $1/T_M$ is a straight line whose slope can be used to calculate the activation energy of desorption.

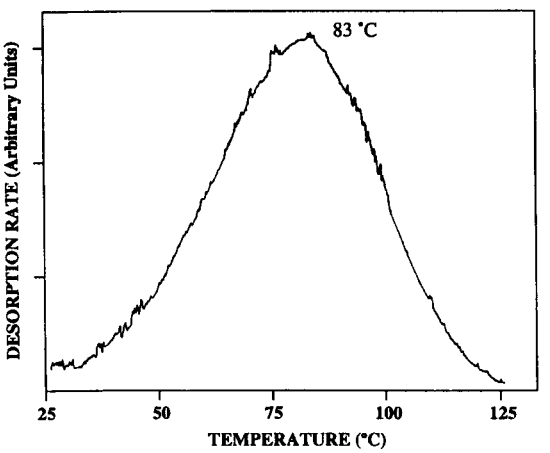

Fig. 9 TPD curves of crystal violet from silica gel. N_0=1.26·10^{-7} mol; β=3.20°C min^{-1}; F=8.0 cm^3 min^{-1}; w=0.0350 g

Figure 9 shows the TPD curve in the liquid phase for crystal violet from silica gel at a heating rate of 3.20°C min^{-1}. The Figure shows a single maximum at the relatively low temperature of 83°C. The values of the temperature of the maximum obtained at other heating rates are shown in Table 1.

Table 1 Thermogrammed desorption of crystal violet from silica gel at different heating rates

β/°C min^{-1}	T_M/°C
1.35	67
1.73	73
2.13	78
3.20	83
3.83	89

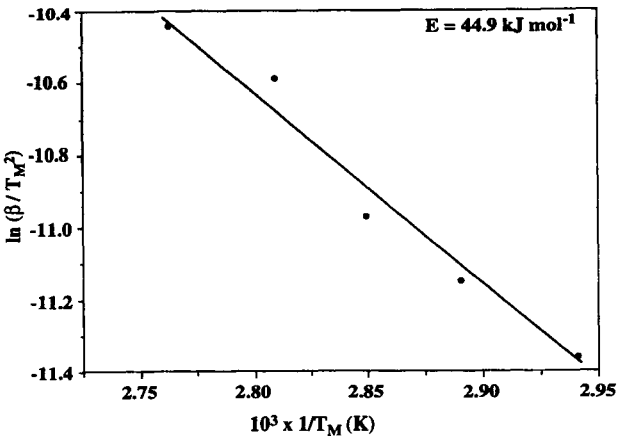

Fig. 10 Determination of activation energy of desorption of crystal violet from silica gel by TPD

The plot of $\ln(\beta/T_M^2)$ *vs.* $1/T_M$ is shown in Fig. 10. Calculation of the activation energy from the slope furnished a value of 44.9 kJ mol^{-1}. This value agrees with that obtained previously in the CRTD study. On comparing the two procedures, the fact that it is possible to obtain the activation energy in CRTD from a single experiment is striking. Additionally, treatment of the experimental data is very simple.

Simple desorption from two adsorption sites

Working with the apparatus in the TPD mode, we obtained the desorption curve of the dye C.I. direct green 26 from mercerized cotton (Fig. 11). The heat-

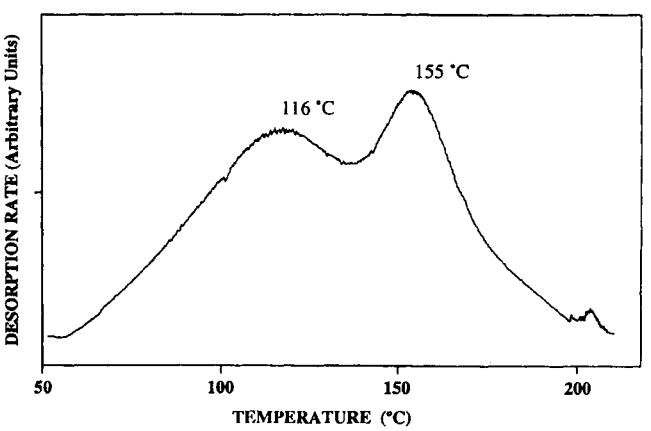

Fig. 11 TPD curves of solophenyl green from mercerized cotton. N_0=5.05·10^{-7} mol; β=3.20°C min^{-1}; F=7.0 cm^3 min^{-1}; w=0.0500 g

ing rate was 3.20°C min^{-1} and the flow rate of the carrier liquid, water, was 7.0 cm^3 min^{-1}. The sample size was 0.1242 g. The TPD curve has two peaks with maxima centred at 116 and 155°C, indicating the existence of two different adsorption sites with different energies. Accordingly, this system dye/cotton was chosen to check the desorption model at constant rate from two active sites.

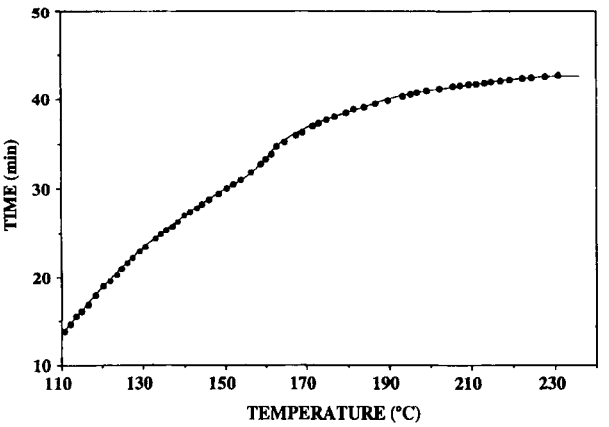

Fig. 12 CRTD heating curve of C.I. direct green 26 from mercerized cotton. N_0=1.25·10^{-6} mol; β=3.20°C min^{-1}; F=6.0 cm^3 min^{-1}; C=2.9·10^{-8} mol min^{-1}; w=0.1242 g

Figure 12 shows the heating curve of the CRTD experiment at a constant desorption rate of 2.9·10^{-8} mol min^{-1}, carried out with 0.1242 g of sample and a flow rate of 6.0 cm^3 min^{-1}. The step corresponding to desorption from the second adsorption site is seen quite clearly.

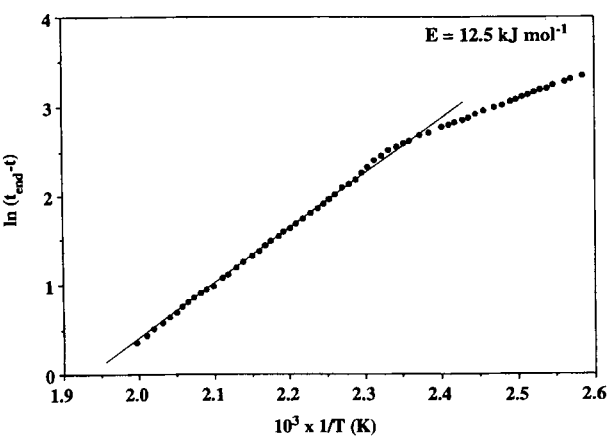

Fig. 13 Determination of activation energy of desorption of C.I. direct green 26 from mercerized cotton by CRTD

According to the proposed model, it is possible to determine the activation energy of the second adsorption site by plotting $\ln(t_{end}-t)$ *vs.* $1/T$ (Eq. (14)). Figure 13 shows this plot. Fitting of the stretch of the second desorption site to a straight line permits calculation of the activation energy from the slope of the straight line. The value of this energy proved to be 12.5 kJ mol^{-1}.

Conclusions

The differences and advantages involved in carrying out thermal desorption either with a programmed temperature, TPD, or at constant rate, CRTD, are patent in the results obtained; in the case of CRTD, greater simplicity is achieved.

From the experimental point of view, the suitability of a TPD set-up for working in the CRTD mode involves no extra complications.

Since one is working at a constant desorption rate, desorption takes place in a completely homogeneous way throughout the experiment. By contrast, in the TPD experiments the desorption rate varies continuously and at certain times of desorption the appearance of other phenomena such as diffusion control, readsorption, etc., may be favoured.

Another advantage of the CRTD experiments is that the values of the magnitudes being recorded, time and temperature, lie within a very broad range and may be measured with great precision.

From the point of view of the equations describing desorption, these are simpler for CRTD than for TPD. CRTD requires only two variables to describe desorption, t and T, which are measured directly during the experiment. By contrast, the desorption rate equation for TPD has three variables, v, N and T (Eq. (1)) and, although it may be transformed into another equation with only two variables (Eq. (2)), this is a differential equation without an exact integration.

Another of the advantages in the use of CRTD is the lower number of experiments required to obtain the kinetic parameters, with the subsequent saving of time. Thus, the activation parameters A and E are determined from a single experiment, while in TPD a whole series of experiments at different heating rates is required.

Additionally, the kinetic order of the desorption process can readily be calculated from two CRTD experiments. In TPD, no procedure that will allow the specific determination of the kinetic order of desorption has hitherto been described.

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