BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (1), 85—89 (1978)

Analysis of Thermal Desorption Curves for Heterogeneous Surfaces. I. A Linear Variation of the Activation Energy of Desorption

Yasuo Tokoro, Makoto Misono, Toshio Uchijima, and Yukio Yoneda
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received June 17, 1977)

This paper deals with the analysis of the desorption curves for heterogeneous surfaces, where the activation energy of desorption, E_d, linearly depends on surface coverage, θ, *i.e.*, $E_d=E_d^0+\alpha(1-\theta)$. Computer simulation resulted in a characteristic change of curve shapes corresponding to the variation of desorption rate parameters, E_d^0, A, and α. By means of empirical parameters characterizing the peak shapes such as peak temperature, half width and symmetry factor, we were able to obtain a set convenient and valid equations for estimating the rate parameters. The curve fitting method was also investigated and found to be more precise, the equations obtained being very useful for giving an initial set of values for this method. The two methods were applied to the thermal desorption curves of CO_2 on TiO_2, and found to be useful and reliable.

The thermal desorption technique, employing a continuous rise of temperature, has been widely used for studies of chemisorbed states on metal surfaces. Thermal desorption curves have been discussed in terms of the reaction order and the activation energy of desorption from the different surface sites or crystal planes.

The technique has been getting familiar in the field of catalysis on oxides and others. The variations of temperature, area and number of the thermal desorption peaks before and after certain treatments and/or chemical reactions were studied, and discussed qualitatively in relation to the nature of reaction sites and the reaction mechanism. Halpern and Germain[1] have reported interesting results in which the values of activation energy obtained from the thermal desorption curves of oxygen on transition metal oxides are correlated to the catalytic activities for oxidation on the oxides. Although their method for analysis is not so reliable, this kind of application is of interest from the viewpoint of characterization of catalysts.

The thermal desorption curves usually show some multiple peaks and complicated shapes, which is supposed to be due to surface heterogeneity, induced or intrinsic. The surface heterogeneity is expected to play an important role in catalysis. It is desirable to express the desorption energy as a function of surface coverage by quantitative analysis of the thermal desorption curves.

The analyses for homogeneous surface have been reported by Redhead,[2] Cvetanović, and Amenomiya[3] and Lord and Kittelberger.[4] An accurate method, discussed in detail by Cvetanović, is to compare the shifts of the peak maximum temperatures, T_m, of the thermal desorption curves with widely differing heating rates, β, where the slope of $\ln(T_m^2/\beta)$ against T_m gives the activation energy of desorption E_d for the first order desorption.

There are a few reports on the analysis of thermal desorption curves for heterogeneous surface. Hobert and Knappe[5] simulated the desorption curves in the case where E_d changes linearly with coverage. Dawson and Peng[6] assumed the same kind of heterogeneity for the λ state nitrogen on tungsten surface, and determined the rate parameters by the curve fitting method, but there remains a problem about the uniqueness of their solution.

We have investigated how the shapes of the desorption curves change by varying the rate parameters widely and systematically in the heterogeneous case where E_d decreases linearly with coverage. The variation of rate parameters leads to the characteristic change of the curve shapes. In turn, the empirical curve parameters can be correlated well with the rate parameters. The relation gives convenient equations to estimate the rate parameters from experimental desorption curves. The curve fitting method was also examined to determine the rate parameters on the heterogeneous surface with the linear variation of the activation energy of desorption. The analyses were verified to be useful and reliable by applying them to the thermal desorption curves of carbon dioxide on titanium dioxide.

Calculations

In the case where a single adsorbed state exists and no readsorption occurs, the desorption rate is expressed by

$$-\mathrm{d}\theta/\mathrm{d}T = (A(\theta)/\beta)\cdot\theta^n\cdot\exp(-E_d(\theta)/RT), \qquad (1)$$

where β is the heating rate ($T=T_0+\beta t$), θ the surface coverage, *i.e.*, the fraction of the adsorbed species remaining on the surface, n the order of desorption, $A(\theta)$ the frequency factor and $E_d(\theta)$ the activation energy of desorption. In a flow system for thermal desorption, the left side term of Eq. 1 is equivalent to the partial pressure or concentration of desorbed molecules normalized by the experimental constants such as the saturated amount of adsorption, the catalyst volume and the carrier gas flow rate.[3]

In the present paper, we deal with the simple case in which desorption follows the first order kinetics and surface heterogeneity is reflected only in the activation energy of desorption, *i.e.*, $A(\theta)$ is independent of θ, and $E_d(\theta)$ changes with θ as follows:

$$E_d = E_d^0 + \alpha(1-\theta). \qquad (2)$$

This indicates that the activation energy of desorption has a value of E_d^0 at saturation coverage and increases with desorption in proportion to $(1-\theta)$. Equation 1, in which $E_d(\theta)$ is given by Eq. 2, is an ordinary differential equation, which can be solved numerically for different sets of values of A/β, E_d^0 and α. Though β is an experimental parameter independent of A, the reciprocal of β makes an essentially equivalent contribution in Eq. 1. Thus A/β is treated as an independent parameter. Calculations were carried out to simulate the thermal desorption curve with A/β from 10^8 to 10^{16} K^{-1} at 10^2 K^{-1} intervals, E_d^0 from 10 to 45 kcal*/mol in increments of 5 kcal/mol and α from 0 to 20 kcal/mol in increments of 5 kcal/mol. The starting values of T and θ in the calculation were usually 100 K and 1.0, respectively. The value of A is expected to be close to $h/kT \approx 10^{13}$ s^{-1} according to the simple rate theory, but it was changed in the wide range above, the reported values of A for desorption being scattered in the range 10^4—10^{16} s^{-1}.³⁾ Calculations were made on a HITAC 8700/8800 computer. The simulated curves, $-d\theta/dT$ *vs.* T, will be shown in the later section.

Experimental

The thermal desorption curves were obtained by linear temperature increase of the sample using a thermal conductivity cell as a detector. The sample was titanium dioxide (Junsei Kagaku Co.), which had been calcined for 5 h at 500 °C in the air. The pre-adsorption was carried out by letting low pressure carbon dioxide in He flow through the sample bed at room temperature. The gases desorbed from the sample into the carrier gas stream were confirmed to consist of only carbon dioxide with a quadrupole mass spectrometer.

Results and Discussion

Estimation of Rate Parameters. Some simulated curves with a wide range of values of A/β, E_d^0, and α are shown in Fig. 1. The effect of A/β on the curves when E_d^0 and α remain constant is given in Fig. 1(a); as the value of A/β decreases, peak temperature shifts to a higher one, and peak width becomes broader. As the value of E_d^0 increases when A/β and α are constant, the peak shifts to higher temperature, and its width becomes slightly broader (Fig. 1(b)). The effect of α on the curves when A/β and E_d^0 are kept constant is given in Fig. 1(c). With increase in the value of α, the peak temperature does not change so much but its shape changes remarkably into a broad and flat one. The behavior is in accord with the results of Hobert and Knappe.⁵⁾

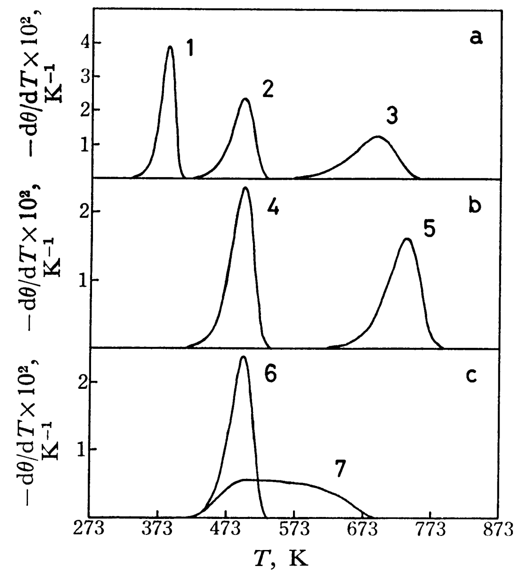

Fig. 1. Simulated thermal desorption curves with various rate parameters. Desorption was treated with the first order kinetics. Numbers in the figures correspond to the rate parameters listed below.

Curve No.		$\log (A/\beta)^{a)}$	$E_d^{0\ b)}$	$\alpha^{c)}$
a	1	16	30	0
	2	12	30	0
	3	8	30	0
b	4	12	30	0
	5	12	45	0
c	6	12	30	0
	7	12	30	10

a) A/β, K^{-1}. b) kcal/mol. c) kcal/mol.

Table 1. Comparison of calculated peak maximum temperatures with different sets of rate parameters

$T_m^{a)}$	$E_d^{0\ b)}$	$\alpha^{c)}$	$\log (A/\beta)^{d)}$
601	40.0	20.0	14.0
601	31.1	5.0	9.9
601	25.0	10.0	8.1
600	35.1	15.1	12.1

a) K. b) kcal/mol. c) kcal/mol. d) A/β, K^{-1}.

The temperature and shape of the peak are characteristic of a set of values of A/β, E_d^0 and α. This, in turn, affords the possibility that the rate parameters A/β, E_d^0, and α can be determined from the experimental desorption curves, if we choose adequate empirical parameters which characterize their peak shapes.

The peak maximum temperature T_m, the half width D and the symmetry factor γ were chosen as the parameters. The parameter γ is defined as the ratio of the area after and before the peak maximum, and is equivalent to $\theta_m/(1-\theta_m)$, where θ_m is the surface coverage at the peak maximum temperature.

Thermal desorption curves can take almost the same value of T_m with multiple sets of different values of A/β, E_d^0 and α as shown in Table 1. The rate parameters A/β, E_d^0, and α can not be analytically determined by only one empirical parameter, *e.g.* T_m. The effect of the rate parameters on the curves leads to the following results.

T_m changes approximately in proportion to the value of E_d^0 and in inverse proportion to that of $\log(A/\beta)$. The plot, T_m *vs.* $E_d^0/\log(A/\beta)$ gives a roughly linear relation. In the same way, D can be related proportionally to $\alpha/\log(A/\beta)$, and γ to $\alpha \log(A/\beta)/E_d^0$.

These relations hold only roughly with a wide range of values of the rate parameters, and should be refined by introducing other rate parameters and constants. For this, we take the following equations:

$$T_m = (a_1 E_d^0 + a_2 \alpha + a_3)/\log(A/\beta) + a_4, \tag{3}$$

$$D' = (D/T_m^{0.1})^{1.2} = (b_1 E_d^0 + b_2 \alpha + b_3)/\log(A/\beta) + b_4, \tag{4}$$

$$\gamma = (c_1 \alpha \log(A/\beta) + c_2 \alpha + c_3)/E_d^0 + c_4. \tag{5}$$

---

* 1 cal_{th}=4.184J.

Equation 3 and 4 have the same from, but the coefficients of E_d^0 and α differ a great deal from each other. D' in Eq. 4 is used instead of D for correcting the regular deviation from the linear relation in the range of higher T_m. The coefficients of these equations were determined by the least square method. Their values are given in Table 2.

T_m, D', and γ are plotted in Figs. 2, 3, and 4, respectively, against the right side terms of Eqs. 3, 4, and 5 calculated by use of the coefficients in Table 2. The figures show satisfactory straight lines in the range of the given values of the rate parameters. This indicates that the equations are a good approximation to connect the rate parameters with the empirical ones of the desorption curves.

TABLE 2. COEFFICIENTS IN EQS. 3, 4, AND 5

Coefficients in Eq. 3	a_1 191.2	a_2 10.8	a_3 −811.9	a_4 92.2
Coefficients in Eq. 4	b_1 2.2	b_2 308.5	b_3 −85.4	b_4 3.6
Coefficients in Eq. 5	c_1 0.2405	c_2 1.4666	c_3 −1.7301	c_4 0.6524

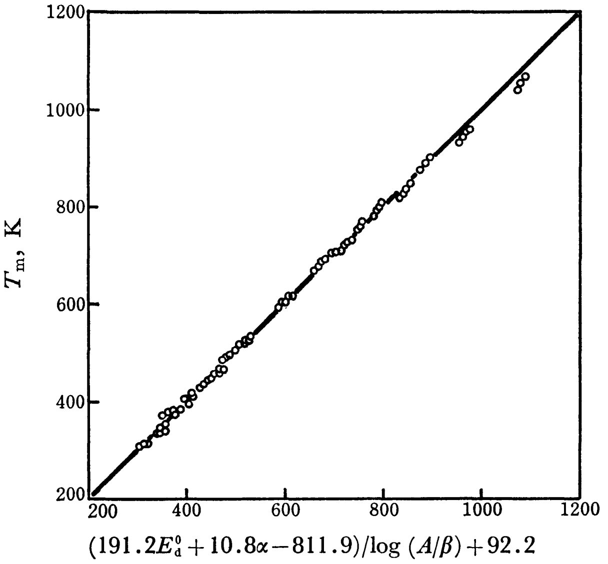

Fig. 2. Correlation of T_m with the right side terms of Eq. 3.

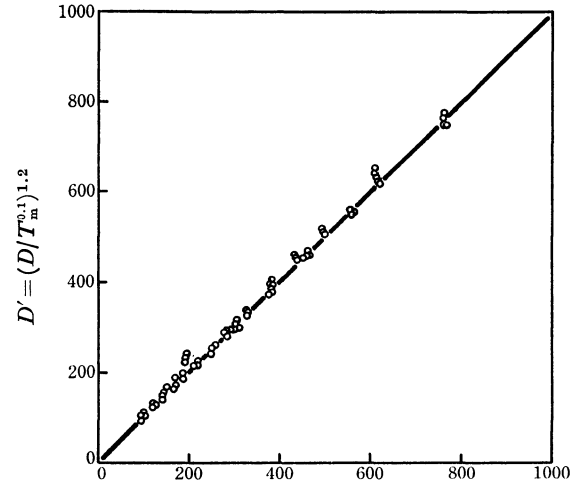

Fig. 3. Correlation of D' with the right side terms of Eq. 4.

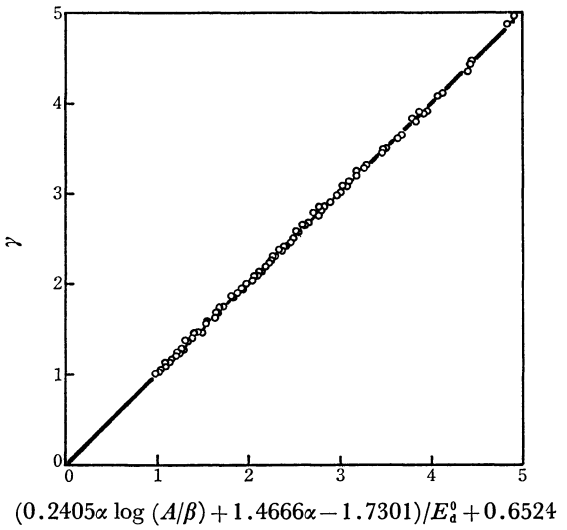

Fig. 4. Correlation of γ with the right side terms of Eq. 5.

The rate parameters should be explicilty expressed by solving these equations. Equations 3, 4, and 5 lead to the relation

$$[\log(A/\beta)]^2 + d_1 \log(A/\beta) + d_2 = 0, \tag{6}$$

where d_1 and d_2 are given by Eqs. 7 and 8, respectively,

$$d_1 = (308.5\gamma' T'_m - 10.8\gamma' D'' + 3.2T'_m - 280.4D'' - 3502.8)/(0.522T'_m - 45.98D''), \tag{7}$$

$$d_2 = (249500\gamma' - 80640)/(0.522T'_m - 45.98D''). \tag{8}$$

The terms γ', T'_m, and D'' are defined as $\gamma'=\gamma-0.652$, $T_m{}'=T_m-92.2$, and $D''=D'-3.6$. In the range of values of the rate parameters used for the simulations, the following relations hold. $300<T_m<1100$, $100<D'<800$, $1<\gamma<6$, $d_1>0$, and $d_2<0$. Consequently, the rate parameters can be estimated by Eqs. 9—11 using the empirical parameters T_m, D', and γ.

$$\log(A/\beta) = (-d_1+\sqrt{d_1^2-4d_2})/2 \tag{9}$$

$$E_d^0 = (5.232\times10^{-3}T'_m+1.84\times10^{-4}D'')\log(A/\beta) + 3.97, \tag{10}$$

$$\alpha = (-3.68\times10^{-5}T'_m+3.243\times10^{-3}D'')\log(A/\beta) + 0.25. \tag{11}$$

The values of the rate parameters thus estimated are compared with the true ones used for the simulations. Some examples are given in Table 3. The deviations of the estimated values from the true ones are less than 10%. Thus, Eqs. 9—11 afford a convenient and reliable method for the estimation of the rate parameters from a single desorption curve.

Two restrictions should be pointed out concerning the applicability of the equations. (1) The equations were derived on the basis of first order desorption of a

Table 3. Comparison of the true values of the rate parameters with those estimated by Eqs. 9—11

True values						
E_a^0 a)	15.0	20.0	25.0	30.0	35.0	40.0
α b)	10.0	15.0	10.0	20.0	15.0	10.0
$\log(A/\beta)$ c)	10.0	12.0	16.0	14.0	8.0	12.0
Empirical parameters						
T_m d)	313	353	336	457	831	679
D e)	207	259	141	302	280	196
γ	3.12	3.88	2.77	3.78	1.59	1.69
Estimated values						
E_a^0 a)	16.5	21.1	25.4	30.4	37.1	42.1
α b)	10.2	15.0	9.9	19.5	15.1	10.1
$\log(A/\beta)$ c)	10.4	11.9	16.4	13.3	8.3	12.2
Percentage error						
E_a^0, %	+10.0	+5.5	+1.6	+1.3	+6.0	+5.3
α, %	+2.0	0.0	−1.0	−2.5	+0.7	+1.0
$\log(A/\beta)$, %	+4.0	−0.8	+2.5	−5.0	+3.8	+1.7

a) kcal/mol. b) kcal/mol. c) A/β, K^{-1}. d) K. e) K.

single adsorbed state from the heterogeneous surface with the linear variation of the activation energy of desorption. (2) The values of the rate parameters were examined in such range as $10 < E_a^0 < 45$ kcal/mol, $5 < \alpha < 20$ kcal/mol and $10^8 < A/\beta < 10^{16}$ K^{-1}.

When the thermal desorption curve has multiple peaks, high resolution between peaks is required for the application of this analysis. It is possible to resolve peaks to a certain extent by large increase of β, although some practical difficulties are encountered.

The desorption order can be determined by the symmetry of the peak in the case of a homogeneous surface, but there are no such means in the case of a heterogeneous one. It is necessary to confirm the desorption order by other measurements.

Curve Fitting Method. The curve fitting method was also investigated for obtaining a more accurate solution. We used the Powell method in order to solve a number of simultaneous equations derived after integration of the differential Eq. 1, the convergence being judged by the summation of squares of differences between the observed and calculated curves.

Even if the summation reaches a minimum in such a nonlinear least square method, it does not always mean the global minimum. In order to get the real solution, a global minimum should be found by widely changing the initial values of the rate parameters. This is the case for thermal desorption, since nearly the same curve could be sometimes reproduced with multiple sets of different values of the rate parameters.

The estimated values would be useful as the initial input values for the application of the curve fitting method, since they are very close to the true values. The curve fitting method was applied to several simulated curves with the result that the values of the rate parameters obtained agreed satisfactorily with the true ones. When the estimated values were used as initial inputs, the calculated result converged more easily to the global minimum. This demonstrates that Eqs. 9—11 are effective not only as a simple method for estimation but also as a method giving good initial input values for the curve fitting calculation.

Application to the Desorption of Carbon Dioxide on Titanium Dioxide. The thermal desorption curve of carbon dioxide from titanium dioxide is shown in Fig. 5. Desorption of carbon dioxide should follow first order kinetics since its dissociative adsorption is very unlikely. The first order thermal desorption from a homogeneous surface is known to give an unsymmetrically shaped curve, but the observed curve has a nearly symmetrical shape. This indicates that the desorption should be treated as one from the heterogeneous surface. The above two methods were applied to this case. The values of the rate parameters obtained by the analysis are compared in Table 4. The two methods give almost the same results, and the calculated curves using the above values reproduce the observed one as shown in Fig. 5.

As a result, the two methods were verified to be effective for getting reliable values of the rate parameters by analyzing a single desorption curve.

There are many complicated cases which can not be treated as such simple heterogeneity. The methods should be extended to analyze a more general heterogeneous surface.

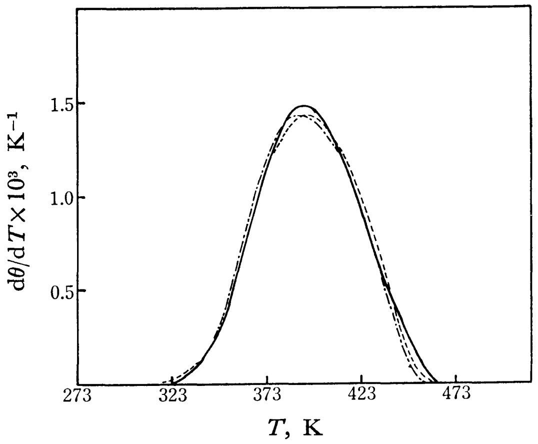

Fig. 5. Observed and calculated thermal desorption curves of carbon dioxide on titanium dioxide: (——) observed; (—•—) calculated using estimated values; (---) calculated by curve fitting method.

Table 4. Rate parameters obtained from the thermal desorption curve of carbon dioxide on titanium dioxide ($\beta = 0.3$ °C/s) by Eqs. 9—11 and the curve fitting method

	Estimated values	Curve fitting method
E_a^0 a)	24.4	22.4
α b)	3.2	2.7
$\log A$ c)	12.4	11.1

The observed values of T_m, D, and γ are 393 K, 66 K, and 1.128, respectively. a) kcal/mol. b) kcal/mol. c) A, 1/s.

Financial support in part by the Kawakami Foundation is gratefully acknowledged.

References

1) B. Halpern and J. E. Germain, *J. Catal.*, **37**, 44 (1975).
2) P. A. Redhead, *Vacuum*, **12**, 203 (1962).
3) R. J. Cvetanović and Y. Amenomiya, *Adv. Catal.*, **17**, 103 (1967).
4) F. M. Lord and J. S. Kittelberger, *Surf. Sci.*, **43**, 173 (1974).
5) H. Hobert and B. Knappe, *Kinet. Katal.*, **13**, 1060 (1972).
6) P. T. Dawson and Y. K. Peng, *Surf. Sci.*, **33**, 565 (1972).