

## FLASH DESORPTION ACTIVATION ENERGIES: DCOOH DECOMPOSITION AND CO DESORPTION FROM Ni (110)

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Accurate values of activation energies were measured by flash desorption methods without assumptions about preexponential factors, reaction orders or specific reaction mechanisms. The activation energies were determined by two methods; one method employed a relationship for the shift in peak temperature with change in heating rate, and the other utilized the change in peak amplitude with shift in peak temperature for different heating rates. Agreement between the two methods was *excellent*. A series of flash curves at different heating rates were obtained for the CO<sub>2</sub> and CO products from DCOOH flash decomposition following adsorption on Ni (110) at 37°C. Adsorbed DCOOH decomposed autocatalytically with an activation energy of 26.6 kcal/mol to form CO<sub>2</sub> and D<sub>2</sub>. Carbon monoxide formation from DCOOH decomposition, which corresponded identically to CO desorption from this surface, showed a first order activation energy of 32.7 kcal/mol; this activation energy was used to fit a series of CO flash desorption curves obtained for CO adsorption at –55°C. The preexponential factor was found to be  $8.5 \times 10^{15} \text{ s}^{-1}$ . The desorption was first order with a slightly coverage dependent desorption energy. In addition the CO flash curves showed additional binding states at coverages at which changes in isosteric heats of adsorption have been observed. The results illustrate the sensitivity of flash desorption for the determination of binding energies over a wide range of coverages.

### 1. Introduction

In order to completely specify the kinetics of surface reactions, including desorption kinetics, it is important to accurately determine both the activation energy and the preexponential factor for the process. Since errors of the order of a few kilocal-

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ories in the activation energy measurement can produce order of magnitude errors in the preexponential factor, it is important to develop accurate means for measuring the activation energy.

In this paper we present an analysis for the graphical determination of activation or desorption energies for surface reaction from flash desorption/decomposition curves at a series of heating rates for the same initial coverage. This analysis is an extension of that of Redhead [1] and develops the relationships between peak amplitude, peak temperature and heating rate. Following the analysis the flash desorption/decomposition behavior of CO and HCOOH on Ni (110) is discussed.

A shorthand notation was used to discuss product desorption following adsorption of gases. The notion  $A(\alpha)/B(T)$  refers to the desorption of the  $\alpha$  peak of gas A following adsorption of gas B at temperature  $T$  in  $^{\circ}\text{C}$ .

## 2. Experimental

The previously described stainless steel ultrahigh vacuum chamber contained a quadrupole mass spectrometer and four-grid LEED–Auger optics [2, 3]. For maximum sensitivity all gases were flashed directly into the mass spectrometer. Because of the system's high pumping speed the flash desorption mass spectrometer signal was directly proportional to the desorption rate from the surface.

The nickel (110) sample was cleaned by argon ion bombardment and annealing at  $500^{\circ}\text{C}$  until a clean Auger spectrum was obtained. The sample was heated at a constant rate by radiation from a tungsten filament, and the temperature was measured by a chromel–alumel thermocouple spot welded to it. This heating rate could be varied over two orders of magnitude by changing the regulated current to the tungsten filament.

Flash desorption measurements for CO were performed by (1) holding the tungsten filament well above the desorption temperature for CO on tungsten and then increasing the filament current suddenly, and (2) allowing the filament to adsorb CO before the flash. In the latter case CO desorbed from the filament in a short burst and did not interfere with the nickel CO peaks. Both methods above yielded identical results. The DCOOH was purified as described elsewhere [3], and the CO used was Matheson Research Purity (99.99%).

Formic acid was exposed to the surface through a stainless steel dosing syringe directed at the surface. Carbon monoxide was admitted to the system through a variable leak, and CO adsorption was carried out at pressures from  $1 \times 10^{-9}$  Torr to  $4 \times 10^{-9}$  Torr. The gas phase CO was pumped away before flashing the sample.

## 3. Theory

The activation energy for a first order flash desorption curve is usually obtained

by substituting the peak temperature into eq. (1) and assuming the preexponential factor equals  $10^{13} \text{ s}^{-1}$  [1]

$$E/RT_p^2 = (\nu/\beta) \exp(-E/RT_p) \quad (1)$$

where  $E$  = activation energy (cal/mol),  $R$  = gas constant,  $T_p$  = temperature at which the desorption rate was a maximum ( $^{\circ}\text{K}$ ),  $\nu$  = preexponential factor ( $\text{s}^{-1}$ ), and  $\beta$  = heating rate ( $^{\circ}\text{K s}^{-1}$ ). This equation is valid for a linear heating rate,

$$T = T_0 + \beta t, \quad (2)$$

where  $T$  = temperature ( $^{\circ}\text{K}$ ),  $T_0$  = initial temperature ( $^{\circ}\text{K}$ ), and  $t$  = time since start of flash (sec).

Redhead suggested a method to obtain  $E$  without assuming a value for  $\nu$  by varying  $\beta$  and plotting  $\log T_p$  as a function of  $\log \beta$ . The activation energy could then be determined from the slope according to eq. (3)

$$(E/RT_p) + 2 = d(\log \beta)/d(\log T_p). \quad (3)$$

The preexponential factor could then be obtained from eq. (1). According to eq. (3) a plot of  $\log \beta$  versus  $\log T_p$  is not a straight line since the slope is dependent on  $T_p$ . Thus an accurate determination of  $E$  is difficult from this plot.

Booth [4] applied a similar method of heating rate variation to calculate electron trap depths for a first order thermoluminescence curve. He obtained peak maxima at two heating rates and calculated the energy depth from these two points. Ehrlich [5] derived a similar expression for flash desorption from eq. (1),

$$\frac{E}{R} \left[ \frac{1}{T_p^{(2)}} - \frac{1}{T_p^{(1)}} \right] = \ln \frac{\beta^{(1)}}{\beta^{(2)}} + 2 \ln \frac{T_p^{(2)}}{T_p^{(1)}} \quad (4)$$

where the superscripts refer to the values of  $T_p$  and  $\beta$  at the two heating rates. Because only two points are used, this is not an accurate method for determining activation energies.

A procedure is presented here which is applicable to desorption rates of non-negative order and surface reactions of the general kinetic form

$$N = -dc/dt = \nu g(c) \exp(-E/RT), \quad (5)$$

where  $N$  = desorption rate (molecules/ $\text{cm}^2 \cdot \text{sec}$ ),  $c$  = surface coverage (molecules/ $\text{cm}^2$ ),  $\nu$  = preexponential factor,  $g(c)$  = arbitrary non-negative order expression for dependence of rate on surface coverage.

For non-zero order desorption with constant  $E$ , eq. (6) was obtained by setting  $dN/dt$  equal to zero at  $T_p$ ,

$$\frac{E}{RT_p^2} = \frac{\nu}{\beta} \left( \frac{dg(c)}{dc} \right)_{T_p} \exp \left( -\frac{E}{RT_p} \right), \quad (6)$$

where  $dg(c)/dc$  is evaluated at  $T_p$ . Then,

$$\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left[ \frac{R\nu}{E} \left( \frac{dg(c)}{dc} \right)_{T_p} \right] - \left( \frac{E}{R} \right) \left( \frac{1}{T_p} \right). \quad (7)$$

A plot of  $\ln(\beta/T_p^2)$  versus  $(1/T_p)$  for a series of heating rates is a straight line with slope  $(-E/R)$ , since the first term on the right side of eq. (7) is independent of  $\beta$ ,  $g(c)$  is only a function of  $c$ , and  $(dg(c)/dc)_{T_p}$  is a function of  $c_p$  alone, which, as shown below, depends only on  $c_0$  provided the desorption or reaction mechanism does not change with heating rate. Thus a linear relationship between  $\ln \beta/T_p^2$  and  $1/T_p$  exists provided the initial coverage is the same for each curve. Thus the activation energy can be determined *independent of reaction order and preexponential factor*. Some specific cases are considered below.

For  $n$ th order desorption ( $n > 0$ ),  $g(c) = c^n$  and eq. (6) becomes

$$\frac{E}{RT_p^2} = \frac{n\nu_n}{\beta} c_p^{n-1} \exp\left(-\frac{E}{RT_p}\right), \quad (8)$$

where  $c_p$  is the surface coverage at the peak temperature,  $T_p$ . It can be shown by integration of eq. (5) from  $T_0$  to  $T_p$  and use of eq. (8) that for constant  $E$

$$c_p^{n-1} = n^{-1} c_0^{n-1}, \quad c_p = c_0^{1/n} \text{ for } n = 1, \quad (9)$$

where  $c_0$  = initial surface coverage (molecules/cm<sup>2</sup>). Eq. (9) was derived assuming that  $E/2RT \gg 1$  so that the approximation was used that [1]

$$\int_{T_0}^{T_p} \exp\left(-\frac{E}{RT}\right) dT = \frac{R}{E} T_p^2 \exp\left(-\frac{E}{RT_p}\right). \quad (10)$$

Then combining eqs. (8) and (9) yields

$$\frac{E}{RT_p^2} = \frac{\nu_n c_0^{n-1}}{\beta} \exp\left(-\frac{E}{RT_p}\right). \quad (11)$$

Eq. (11) can also be shown to be valid for  $n = 0$  by direct integration of eq. (5) and use of eq. (10). Eq. (11) can be written as

$$\ln(\beta/T_p^2) = \ln(R\nu_n c_0^{n-1}/E) - E/R(1/T_p), \quad (12)$$

and since  $\ln(R\nu_n c_0^{n-1}/E)$  is constant for constant initial coverage, a plot of  $\ln(\beta/T_p^2)$  versus  $(1/T_p)$  is a straight line with slope  $(-E/R)$ .

An equation similar to eq. (12) can be derived for a first order desorption with coverage dependent activation energy

$$E = E_0 - \gamma\theta, \quad (13)$$

where  $E_0$  = activation energy at zero coverage (cal/mol),  $\gamma$  = constant (cal/mol), and  $\theta$  = fractional surface coverage. The error in assuming  $\ln(\beta/T_p^2)$  versus  $1/T_p$  to be linear was calculated to be less than one percent for  $\gamma = 4$  kcal/mol.

The mechanism for the surface explosion of formic acid on Ni(110) [3] was given by eq. (5) with

$$g(c) = \frac{c}{c_0} (c_0 - c + fc_0), \quad (14)$$

where  $f$  was a constant less than unity. For this mechanism eq. (7) becomes

$$\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left[ \frac{R\nu}{E} \left( 1 + f - \frac{2c_p}{c_0} \right) \right] - \left( \frac{E}{R} \right) \left( \frac{1}{T_p} \right), \quad (15)$$

and the method of heating rate variation was applicable.

The activation energy can also be determined from the series of flash curves at different heating rates *without knowledge of the heating rate values* since each peak maximum corresponds to the rate at its peak temperature  $T_p$  for the *same surface coverage*. For each curve at  $T = T_p$ ,  $N = N_p$  (amplitude of desorption curve), so that eq. (5) becomes

$$\ln (N_p) = \ln (\nu g(c_p)) - \left( \frac{E}{R} \right) \left( \frac{1}{T_p} \right). \quad (16)$$

A plot of  $\ln N_p$  versus  $1/T_p$  is a straight line with slope  $(-E/R)$ , if  $c_p$  is independent of heating rate, as it is for the cases discussed. This plot has the advantage over the previous method in that heating rates do not have to be separately measured. Instead the peak height and peak temperature are obtained directly from the flash curve.

These methods can be applied to flash desorption or flash decomposition curves without assumptions about reaction order, curve shape, or preexponential factor. In particular for first order reactions this eliminates the often used assumption that  $\nu_1 = 10^{13} \text{ s}^{-1}$ .

To obtain accurate activation energies the heating rates must be varied over two orders of magnitude, as suggested by Redhead [1]. Experimentally this was difficult. At low heating rates the signal decreases to the noise level. At sufficiently high heating rates the signal was not proportional to the desorption rate because the duration of the flash was not large with respect to the characteristic pumping time for the system. Thus the range of heating rates used was limited in our system to 0.2 to  $35^\circ \text{K s}^{-1}$  for  $\text{CO}_2(\beta)/\text{DCOOH}$ .

The method of heating rate variation can be difficult to apply to peaks with low saturation coverage because the signal at low heating rates would not be detectable. Also determination of activation energies for a group of peaks can be complicated because the peak separation decreases with increased heating rate. Finally, the possibility that the reaction mechanism for flash decomposition changes with large changes in heating rate must be considered.

However, for a large number of desorptions from and decompositions on surfaces, the method of heating rate variation may provide an excellent technique for measuring activation energies using flash desorption. This method is suited to nonnegative order desorptions and to surface reactions of the kinetic form expressed by eq. (5). It is most easily applied when only one binding state occurs or when binding states are separated in energy and when the flash peaks are not excessively broad.

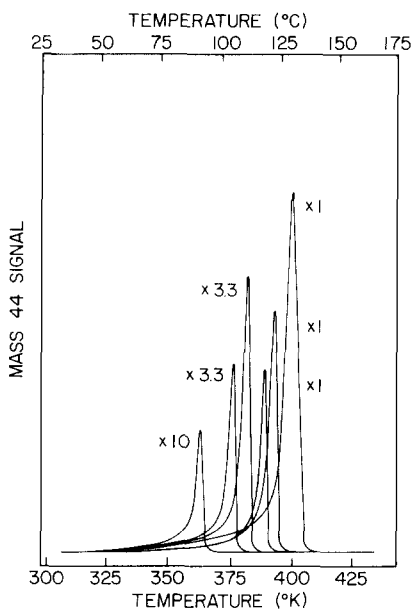


Fig. 1.  $\text{CO}_2/\text{DCOOH}$  (37) flash decomposition spectra at six heating rates for 2 L exposure. Heating rates, starting at the lowest peak temperature, were  $0.30$ ,  $1.2$ ,  $2.0$ ,  $4.0$ ,  $5.7$ , and  $11.0^\circ\text{K s}^{-1}$ .

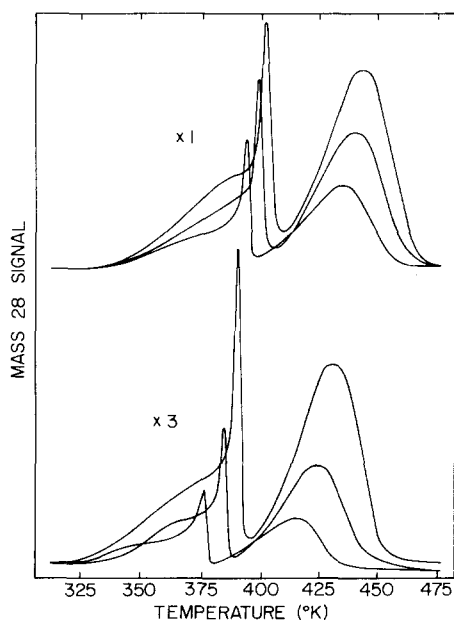


Fig. 2.  $\text{CO}/\text{DCOOH}$  (37) flash decomposition spectra at six heating rates for 2 L exposure. Heating rates, starting at the lowest peak temperature, were  $1.0$ ,  $1.4$ ,  $3.3$ ,  $4.0$ ,  $7.4$ , and  $9.8^\circ\text{K s}^{-1}$ .

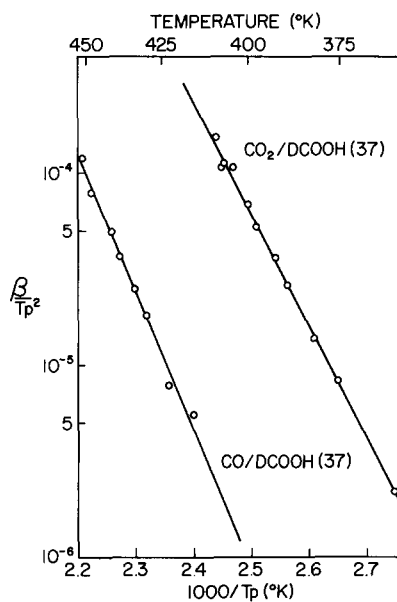


Fig. 3.  $\text{Log } (\beta/T_p^2)$  as a function of  $1/T_p$  for  $\text{CO}_2(\beta)/\text{DCOOH}(37)$  and  $\text{CO}(\alpha_2)/\text{DCOOH}(37)$  for 2 L DCOOH exposure.

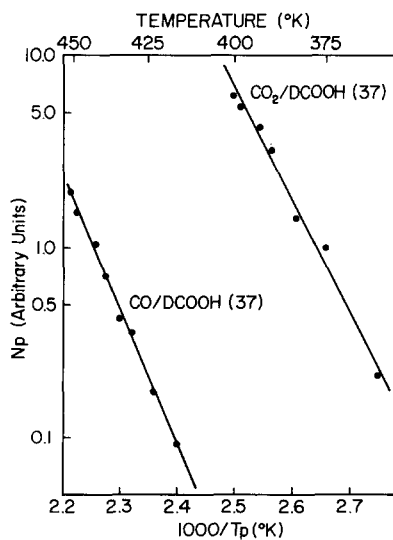


Fig. 4.  $\text{Log } N_p$  as a function of  $1/T_p$  for  $\text{CO}_2(\beta)/\text{DCOOH}(37)$  and  $\text{CO}(\alpha_2)/\text{DCOOH}(37)$  for 2 L DCOOH exposure.

#### 4. Results

A series of  $\text{CO}_2/\text{DCOOH}$  (37) and  $\text{CO}/\text{DCOOH}$  (37) flash decomposition curves were obtained, for two-thirds saturation DCOOH coverage, for heating rates from  $0.3^\circ\text{K s}^{-1}$  to  $35^\circ\text{K s}^{-1}$ . Figs. 1 and 2 show  $\text{CO}_2/\text{DCOOH}$  (37) curves and  $\text{CO}/\text{DCOOH}$  (37) curves respectively for a range of heating rates. As the heating rate was increased the curves shifted to higher temperature and increased in amplitude.

Plots of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  resulted in straight lines for both  $\text{CO}_2(\beta)$  and  $\text{CO}(\alpha_2)/\text{DCOOH}$  (37), as shown in fig. 3. The slopes determined from least squares fits yielded activation energies of  $26.6 \pm 0.5$  kcal/mol for  $\text{CO}_2(\beta)/\text{DCOOH}$  (37) and  $32.8 \pm 1$  kcal/mol for  $\text{CO}(\alpha_2)/\text{DCOOH}$  (37). Greater accuracy was obtained for  $\text{CO}_2$  because the extremely narrow peak signal was detectable at lower heating rates than the CO peak. Plots of  $\ln N_p$  versus  $1/T_p$  for the same series of flash curves also resulted in straight lines, as seen in fig. 4. Least squares fits of these data points gave activation energies of 26.6 kcal/mol for  $\text{CO}_2(\beta)/\text{DCOOH}$  (37) and 32.6 kcal/mol for  $\text{CO}(\alpha_2)/\text{DCOOH}$  (37). *Agreement between the two methods was excellent.*

Over the range of heating rates used the ratio of peak area to  $\beta$  was a constant for both CO and  $\text{CO}_2$ . This ratio was proportional to initial surface coverage for each peak so that changing the heating rate had no effect on the product distribution.

Since previous flash desorption data by Taylor and Estrup [6] and Madden et al. [7, 8] were not sufficiently resolved to allow accurate comparison to theoretical curves,  $\text{CO}/\text{CO}(-55)$  flash desorption spectra were also obtained. Curves for a heating rate of approximately  $9^\circ\text{K s}^{-1}$  are shown in figs. 5 and 6 and their exposures, coverages, and peak temperatures are listed in table 1. Pressures from  $1 \times 10^{-9}$  to  $4 \times 10^{-9}$  Torr were used for adsorption. At a coverage of 0.005 of saturation the spectra consisted of one first order peak, the  $\alpha_2$  peak, at approximately  $175^\circ\text{C}$ . As coverage increased the  $\alpha_2$  peak temperature decreased, reaching  $159^\circ\text{C}$  at saturation. The high tempera-

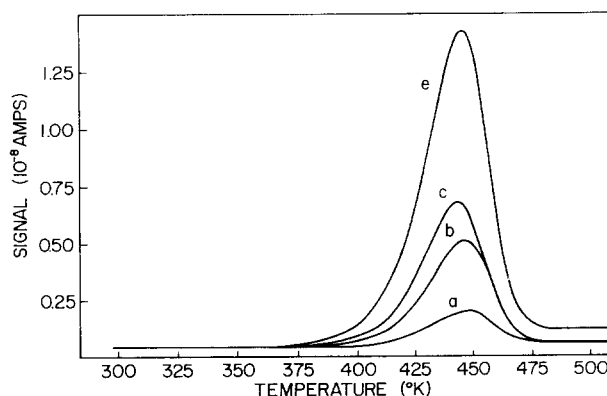


Fig. 5.  $\text{CO}/\text{CO}(-55)$  flash desorption spectra for low coverages (see table 1).



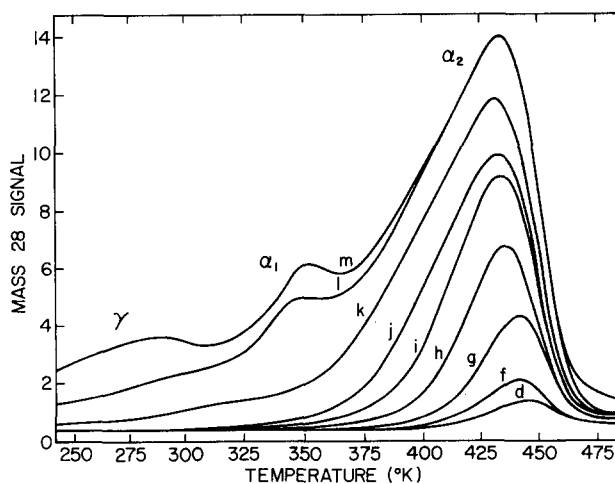


Fig. 6. CO/CO(-55) flash desorption spectra for coverages up to saturation (see table 1).

Table 1  
CO/CO(-55) flash desorption spectra

Curve <sup>a</sup>	Exposure (L)	Fractional coverage	CO( $\alpha_2$ ) curve	
			$T_p$ (°C)	$E$ (kcal/mol)
a	0.005	0.005	175	33.25
b	0.023	0.013	174	33.16
c	0.036	0.018	172	33.01
d	0.063	0.026	172	33.01
e	0.075	0.041	172	33.01
f	0.125	0.048	169	32.78
g	0.25	0.11	168	32.70
h	0.50	0.20	163	32.30
i	0.75	0.32	162	32.22
j	1.0	0.41	161	32.15
k	2.0	0.66	160	32.07
l	4.5	0.95	160	32.07
m	10.0	1.00	159	32.00

<sup>a</sup> Curve labels refer to figs. 5 and 6.

ture side of the  $\alpha_2$  peak did not drop back to the base line, but the amount of gas corresponding to this part of the curve was small and was possibly due to adsorption on other surfaces, such as the sample support wire.

Near saturation two additional peaks appeared in the spectrum. Above 0.7 CO coverage a small first order peak, the  $\alpha_1$  peak, was present at 80°C. Above 0.9 CO coverage an even smaller peak, the  $\gamma$  peak, was observed near 15°C. For high CO coverages some coadsorption of  $H_2$  from the background into the  $H_2(\beta)/H_2(-55)$  state occurred, but it did not appear to effect the shape or location of the CO desorption curve.

## 5. Discussion

The data points in figs. 3 and 4 deviate very little from the lines obtained by least squares fitting. This small deviation and the excellent agreement between the two methods using heating rate measurements and peak height measurements indicate that the technique of heating rate variation yields accurate activation energies for both flash desorption and flash decomposition. The activation energies were obtained independent of reaction order, curve shape, and assumptions about preexponential factors.

The 26.6 kcal/mol activation energy was substituted into a rate expression represented by eq. (14) to obtain a good fit to the  $CO_2(\beta)/DCOOH(37)$  flash decomposition curve. The activation energy was in the range reported by others for formate decomposition. Details of these calculations are reported elsewhere [3].

Eq. (1) yielded a first order preexponential factor of  $8.5 \times 10^{15} \text{ s}^{-1}$  for  $CO(\alpha_2)/DCOOH(37)$  using the average activation energy of 32.7 kcal/mol. A theoretical desorption curve using these values of  $\nu$  and  $E$  is shown in fig. 7. The agreement with

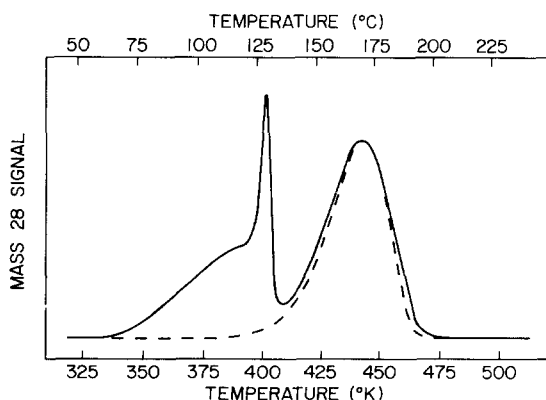


Fig. 7. Comparison of experimental  $CO/DCOOH(37)$  curve (solid line) with theoretical curve for  $CO(\alpha_2)/DCOOH$  (dashed line) for a first order desorption rate constant of  $8.5 \times 10^{15} \exp(-32700/RT)$ .

the  $\text{CO}(\alpha_2)/\text{DCOOH}$  (37) curve is good. The preexponential factor can also be obtained from the  $\nu$ -intercept of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  by use of eq. (7). For  $\text{CO}(\alpha_2)/\text{DCOOH}$  the value of  $\nu$  was within ten percent of that obtained by use of eq. (1). The desorption of  $\text{CO}(\alpha_2)$  was rate limiting for  $\text{CO}(\alpha_2)/\text{DCOOH}$  (37) corresponding to  $\text{CO}(\alpha_2)/\text{CO}(-55)$  at the same coverages. Thus the above values of  $\nu$  and  $E$  were used to fit the  $\text{CO}/\text{CO}(-55)$  flash curves. The activation energies reported previously for CO and  $\text{CO}_2$  formation from  $\text{HCOOH}$  decomposition [2] assumed that the preexponential factor was  $10^{13} \text{ s}^{-1}$ . The heating rate variation calculations show this assumption to be incorrect.

The  $\text{CO}/\text{CO}(-55)$  flash desorption curves were in good agreement with those obtained by others [2, 6, 8]. Taylor and Estrup [6] also observed two desorption peaks and their peak temperatures corresponded to the  $\alpha_1$  and  $\alpha_2$  peaks in fig. 6. Since pumping speeds were not measured for our  $\text{CO}/\text{CO}(-55)$  curves, determination of absolute coverages was not possible. However the coverage versus exposure curve was calibrated assuming the initial sticking probability was unity [2, 6, 8, 9]. This yielded a saturation coverage of  $1.0 \pm 0.2 \times 10^{15} \text{ molecules/cm}^2$ , which was within experimental error of the value of  $1.1 \times 10^{15} \text{ molecules/cm}^2$  reported by others [7, 10]. The coverage versus exposure curve was also similar to that observed by Taylor and Estrup [6, 9].

The  $\text{CO}(\alpha_2)/\text{CO}(-55)$  flash desorption curves shifted to lower peak temperatures with increasing initial coverage, as seen in figs. 5 and 6. The asymmetry of the curves indicated desorption was first order, and the peak shift was too small to yield a reasonable second order activation energy. Thus,  $\text{CO}(\alpha_2)/\text{CO}(-55)$  was apparently first order desorption with a coverage dependent activation energy.

For each  $\text{CO}(\alpha_2)$  peak temperature listed in table 1, eq. (1) was used to calculate an activation energy, assuming  $\nu = 8.5 \times 10^{15} \text{ s}^{-1}$ . The values, listed in table 1, varied from 33.25 to 32.00 kcal/mol and theoretical desorption curves are shown in fig. 8 for comparison. These values corresponded to the activation energies at  $c = c_p$  for each curve. Thus, though fractional coverage,  $\theta$ , varied from 0.005 to 1.0 as listed in table 1,  $\theta$  at the  $\alpha_2$  peak temperature varied from 0.002 to 0.207. The coverage at the peak temperature,  $c_p$ , was proportional to the fraction of the area under the curve that was above the peak temperature. Therefore, the activation energies calculated from the  $\text{CO}(\alpha_2)$  peaks were only for coverages below  $2.1 \times 10^{14} \text{ molecules/cm}^2$ .

Taking  $\nu = 8.5 \times 10^{15} \text{ s}^{-1}$ , the  $\text{CO}(\alpha_1)$  peak had an activation energy of 25.9 kcal/mol. This corresponded to the activation energy at 0.73 fractional coverage. Likewise, the activation energy for the small peak at  $15^\circ\text{C}$ , the  $\text{CO}(\gamma)$  peak, was 21 kcal/mol and corresponded to a fractional coverage of 0.92. The values of these activation energies were consistent with previously published binding energies obtained from isosteric heats [6, 7]. Flash desorption has the additional advantages over isosteric heats of being able to measure activation energies at much lower energies and to determine preexponential factors. Madden et al. [7] measured  $E$  to be  $31 \pm 2$  kcal/mol for  $\theta$  from 0.35 to 0.6. Taylor and Estrup [6] likewise calculated  $E$  as 30 kcal/mol for  $\text{CO}(\alpha_2)$ . The agreement with our  $\text{CO}(\alpha_2)$  variable activation energy of

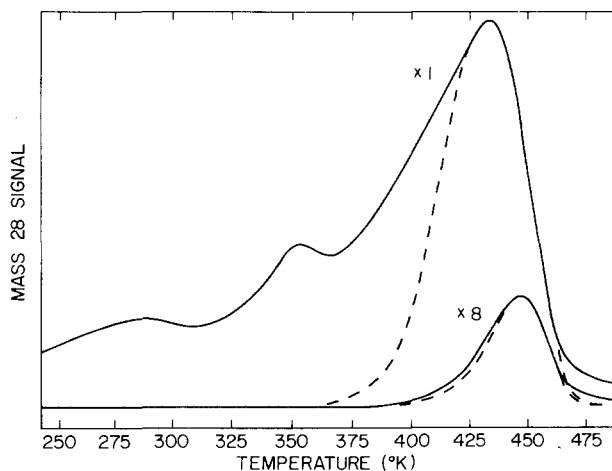


Fig. 8. Comparison of CO/CO(-55) at low coverage and at saturation (solid lines) with theoretical curves for variable activation energy (dashed lines).

32 to  $33 \pm 1$  kcal/mol was excellent. Additionally, at  $\theta$  equal 0.6 to 0.7, Madden et al. saw a rapid drop in isosteric heat to  $25 \pm 2$  kcal/mol. Taylor and Estrup also measured the  $\text{CO}(\alpha_1)$  activation energy as 25.3 kcal/mol. Our value of  $25.9 \pm 1$  kcal/mol at  $\theta = 0.73$  was well within experimental error of these values. Finally, at  $\theta = 0.9$  Madden et al. observed that the isosteric heat decreased rapidly; this was the coverage at which we observed the  $\text{CO}(\gamma)$  peak. In addition, Madden et al. and Taylor and Estrup calculated activation energies from their flash desorption curves for  $\nu = 10^{13} \text{ s}^{-1}$  and obtained values lower than their isosteric heat values. This indicated, as we have calculated, that the preexponential factor was greater than  $10^{13} \text{ s}^{-1}$ . The agreement between flash desorption and isosteric heats indicates that on a homogeneous surface changes in the isosteric heat with coverage cause definite flash desorption peaks.

Hayward and Trapnell [11] state that for transition state theory, in the extreme case where the desorption complex has translational and rotational freedom and the adsorbed molecule does not,  $\exp(\Delta S^\ddagger/R)$  might amount to  $10^3$  or  $10^4$ . The entropy change between the adsorbed state and the activated intermediate corresponds to  $\Delta S^\ddagger$ . Our value of  $8.5 \times 10^2$  for  $\exp(\Delta S^\ddagger/R)$  is thus not unreasonable and corresponds to an entropy change of 13.5 cal/°K/mol for desorption. The rotational entropy for CO gas is 11.3 cal/°K/mol. This implies the transition state has much more freedom than the adsorbed molecule, which is apparently quite rigidly bound.

The results confirm the accuracy of heating rate variation for measurement of activation energies. They also demonstrate the ability of flash desorption to measure binding energies at low coverages where isosteric heats are not easily measured. Additionally, flash desorption was shown to be able to measure small changes (less than 1 kcal/mol) in a coverage dependent activation energy.

## 6. Summary

Two methods for measuring activation energies for flash desorption and decomposition spectra by changing heating rates were presented. Data for  $\text{CO}_2(\beta)/\text{DCOOH}(37)$  and  $\text{CO}(\alpha_2)/\text{DCOOH}(37)$  flash decomposition for two orders of magnitude change in heating rates yielded activation energies of 26.6 and 32.7 kcal/mol respectively. The two methods were consistent and yielded accurate values of activation energies. They eliminated assumptions about reaction order and preexponential factors. These results show the value of flash desorption in *reaction studies* for determination of activation energies by similar means.

Accurate curve shapes were also obtained for  $\text{CO}/\text{CO}(-55)$  flash desorption, and most CO desorbed in the first order  $\alpha_2$  peak with a slightly coverage dependent activation energy. Calculated desorption curves for a preexponential factor of  $8.5 \times 10^{15} \text{ s}^{-1}$  show good agreement with the  $\text{CO}(\alpha_2)$  peak. Above 0.7 coverage a second small desorption peak was observed, with a binding energy of 25.9 kcal/mol. Above 0.9 coverage a third smaller peak with a binding energy of 21 kcal/mol appeared. The activation energies calculated from the flash desorption curves show good agreement with previously published work.

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