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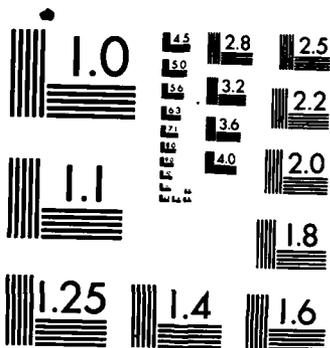
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20. ABSTRACT CONTINUED

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FINAL REPORT

ARO Contract No. 19250-CH

"Organic Functional Group Reactivities at Metal Surfaces"

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I. Problem

This research has been directed toward understanding the mode of surface decomposition of organic functional groups on atomically-clean single crystal metal surfaces. In addition, the development of rapid and efficient kinetic methods to gain this information has been a goal which has been achieved. The stepwise decomposition of methanol and ethanol has been characterized on a Ni(111) single crystal surface. In addition, a Cu(111) surface has been studied for methanol decomposition behavior, and then its surface behavior has been modified systematically by oxygen adsorption.

II. New Kinetic Methods Developed to Study Elementary Reaction Processes on Single Crystal Surfaces**A. Introduction**

One of our primary objectives has been the development of new and efficient research methods based on kinetic measure-

ments and chemical observations to elucidate details of elementary surface processes. Information at this level of inquiry is really necessary before spectroscopic and dynamical investigations of a more detailed type can be carried out effectively. We have used a single apparatus to develop three new surface kinetic measurement methods, which are outlined below.

The deuterium kinetic isotope effect (DKIE) [7] and Scanning Kinetic Spectroscopy (SKS) [8] constitute a powerful combination of chemical probes of the reactive chemistry of functional groups at well-defined surfaces. Threshold Temperature Programmed Desorption (TTPD) is a convenient method for cleanly measuring the coverage dependence of desorption kinetics from surfaces.

B. Apparatus and Experimental Methods

1. Apparatus

Figure 1 shows a drawing of the ultrahigh vacuum apparatus constructed in our laboratories and used for all of the studies described here. The apparatus permits us to direct a collimated molecular beam of an organic reactant onto an atomically clean single crystal surface maintained electrically at any desired temperature above 80K. The absolute flux of the organic beam onto the crystal is known from previous calibration of flow rates through the 2 micron calibrated conductance and from geometrical considerations [9]. Facing the single crystal surface is a shielded and differentially pumped quadrupole mass spectrometer. The geometry of the crystal and the shield permits the study of both the reflected (unreacted) reactant molecules

and desorbing product species originating only from the crystal surface, and avoids spurious effects from crystal edges, support leads, and the vacuum system itself.

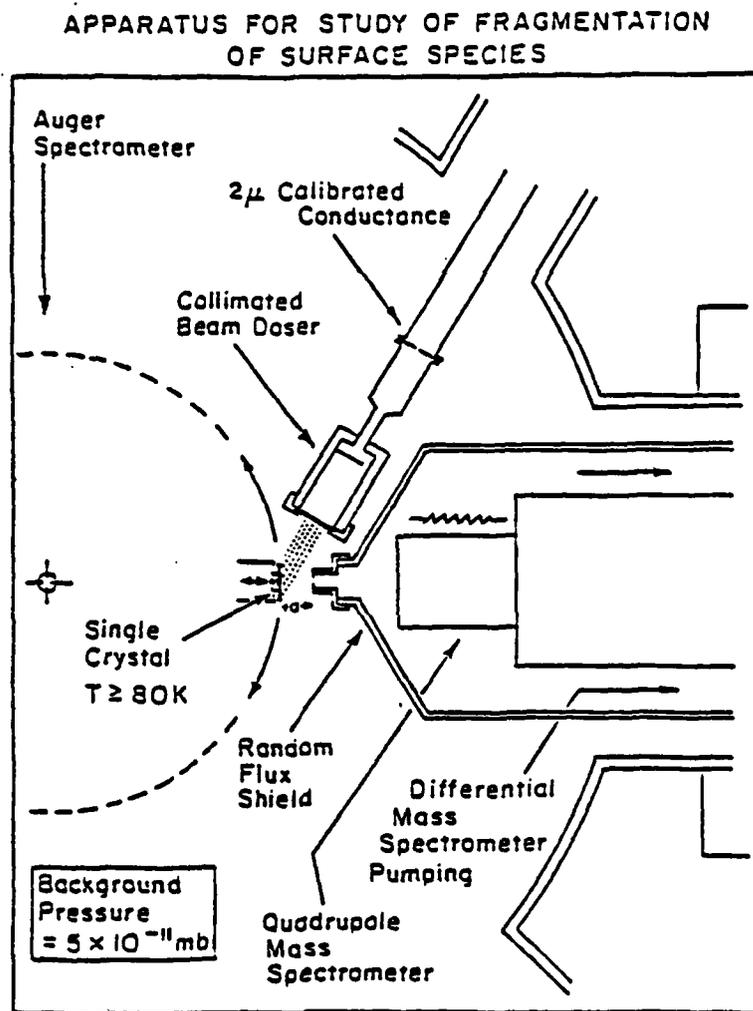


Figure 1.

The reactant beam is incident on the surface at an angle of 60° from the surface normal. Location of the close-coupled QMS detector behind the random flux shield and along the surface normal means that desorbing product species are measured with

rather high efficiency. Desorbing reactant signal is also sampled by the 3 mm sampling orifice. This reactant signal is relatively insensitive to any changes in specular reflected scattering (being 60° from the specular direction), but is very sensitive to the flux of departing reactant molecules which are accommodated on the surface and then desorbed intact. Thus, the geometry shown in Fig. 1 is optimized for the study of surface chemical reactions through mass spectrometric observation of all product species as well as through observation of changes in the yield of unreacted reactant species.

The mass spectrometer is multiplexed so that as many as twelve different mass peaks may be monitored in rapid sequence during an experiment. Typical parameters for multiplexing in the SKS experiment described below would allow five mass species and the crystal temperature to be sampled each once per second, with 0.162 seconds counting time on each mass species.

An important factor motivating this research approach is the high inherent sensitivity of the mass spectrometer detector. Changes in the (reflected) reactant molecule signal corresponding to reaction of about 0.1% of a monolayer (10^{12} cm $^{-2}$) of reactant per second are easily detected. The detection limit for products of surface decomposition reactions is often much better due to favorable geometric and background residual gas conditions.

C. The Deuterium Kinetic Isotope Effect (DKIE)

1. Physical Basis

It has long been recognized in homogeneous chemical kinetics that the influence of deuterium substitution on the

rates of chemical reactions involving hydrogen bond breaking may be utilized in understanding the elementary kinetic processes at work [10]. We have employed this method to cleanly determine the molecular site in a molecule where surface chemical reactivity occurs. This is done by selective labeling with D in various stereochemical positions. D-labeling at the reactive molecular site selectively retards the reaction rate, whereas D-labeling on another molecular site not involved in the molecule's surface

KINETIC ISOTOPE EFFECT Schematic Potential Energy Diagram

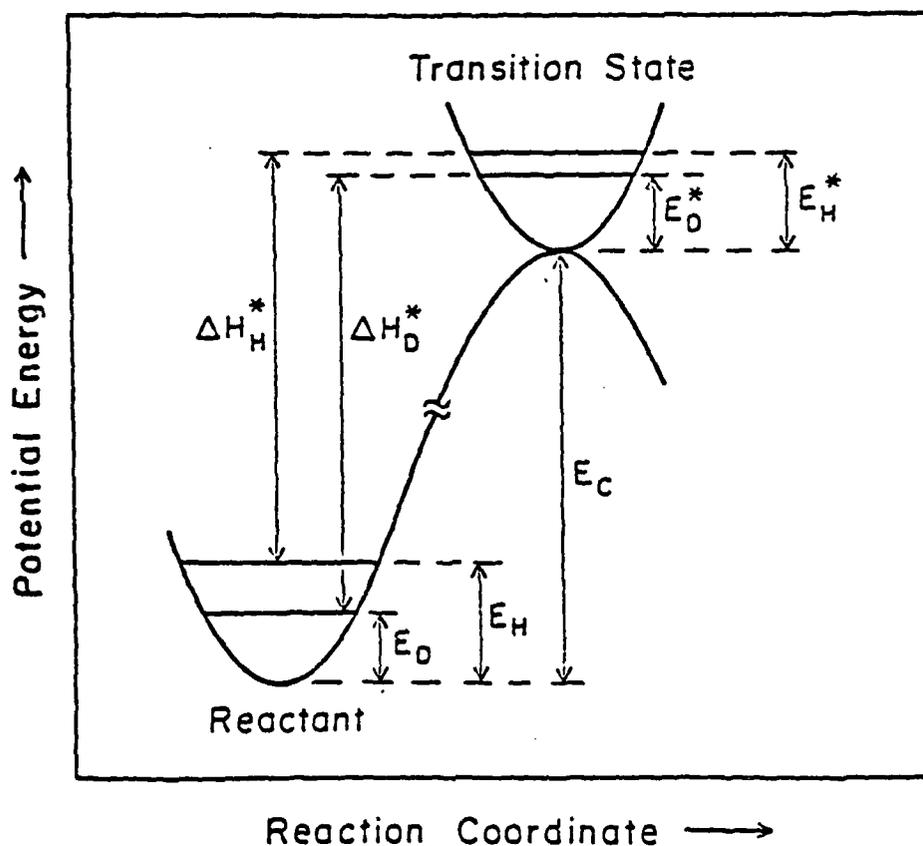


Figure 2.

chemistry is found to have little or no measurable effect on reaction rate. This phenomenon, based on well-known principles relating to zero point vibrational energy differences in both reactants and the transition complex due to D-substitution, has not yet been used widely in surface chemistry studies on single crystal substrates. A schematic diagram showing the difference in ΔH_H^* and ΔH_D^* for a chemical reaction on a surface is shown in Figure 2. Here, for a DKIE to be observed, the molecular site containing D or H must be involved in the reaction pathway leading to hydrogen bond breaking in the surface complex.

Our research has so far shown that the DKIE may be used in three different kinds of surface measurements probing three distinct types of surface reaction processes:

- A DKIE in the zero coverage reactive sticking coefficient (S_O^R) locates that bond site in a molecule which is the initial dissociative chemisorption site.
- A DKIE observed under steady state (SS) reaction conditions can be used to identify the rate determining step in a complex decomposition mechanism on a surface.
- A DKIE, affecting the characteristic decomposition temperature of a surface intermediate may be used to identify elementary surface processes in SKS.

2. Locating the Molecular Site of Chemical Reactivity in Dissociative Chemisorption

As shown in Figure 3, measurements of S_O^R , the reactive sticking coefficient of methanol under zero coverage conditions,

show that deuterium labeling the hydroxyl hydrogen kinetically retards the reactive sticking of methanol on Ni(111) [7]. In contrast to this, it is seen in Figure 3 that deuterium labeling of methyl hydrogen yields no change in S_0^R .

KINETIC ISOTOPE EFFECT
METHANOL/Ni(111): S_0^R , INITIAL REACTIVE
STICKING COEFFICIENT vs. TEMPERATURE

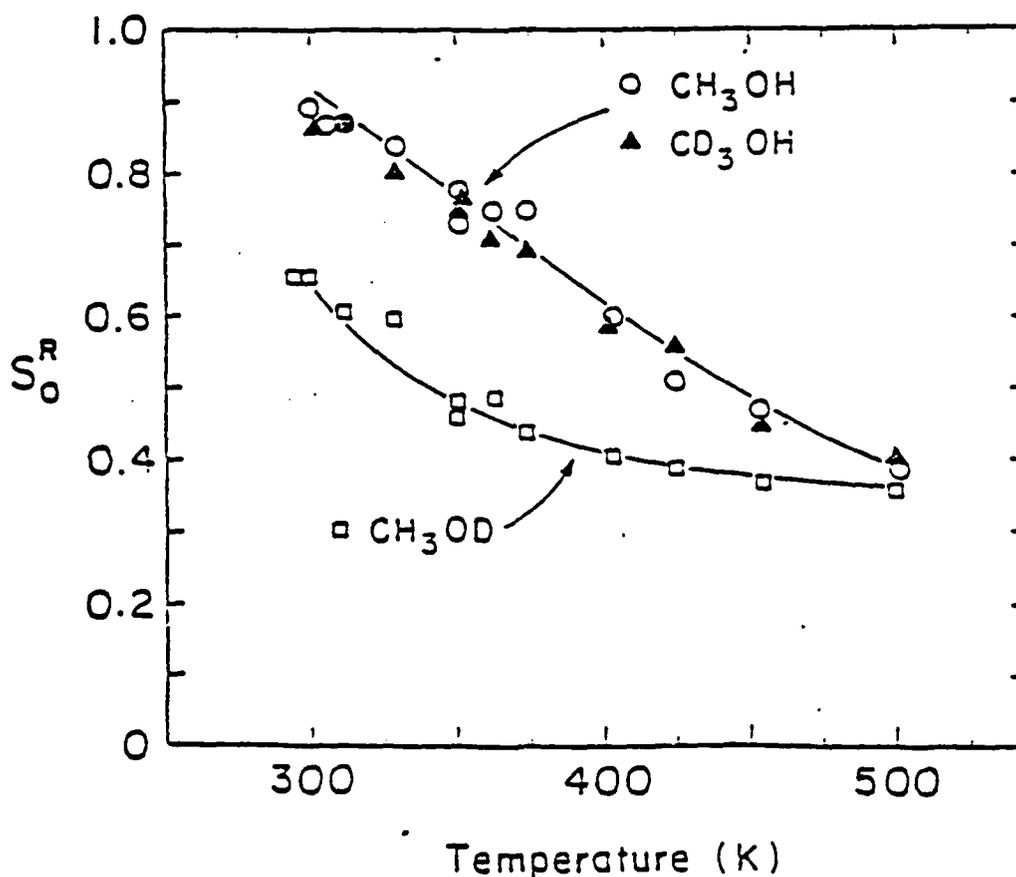


Figure 3.

O-D bond breaking is therefore involved in the rate determining step in methanol decomposition on Ni(111) from 300 - 500K. An unstable $\text{CH}_3\text{O}(\text{a})$ intermediate is therefore indirectly identified

as being involved in the rate controlling step over a wide temperature range from 300 - 500K. This $\text{CH}_3\text{O}(a)$ species may be spectroscopically observed [11,12] only near 200 K. As discussed in detail in reference [7], the magnitude of the observed DKIE may be used to suggest the type of vibrational modes of CH_3OH which becomes the dissociation reaction coordinate controlling the rate of molecular decomposition.

3. Determining the Rate Controlling Step in a Surface Catalyzed Reaction, Operating At Steady State.

Figure 4 shows a plot of reaction rate for methanol decomposition on Ni(111) measured at various temperatures.

METHANOL on Ni(III)
Steady State Decomposition Rate vs. Temperature

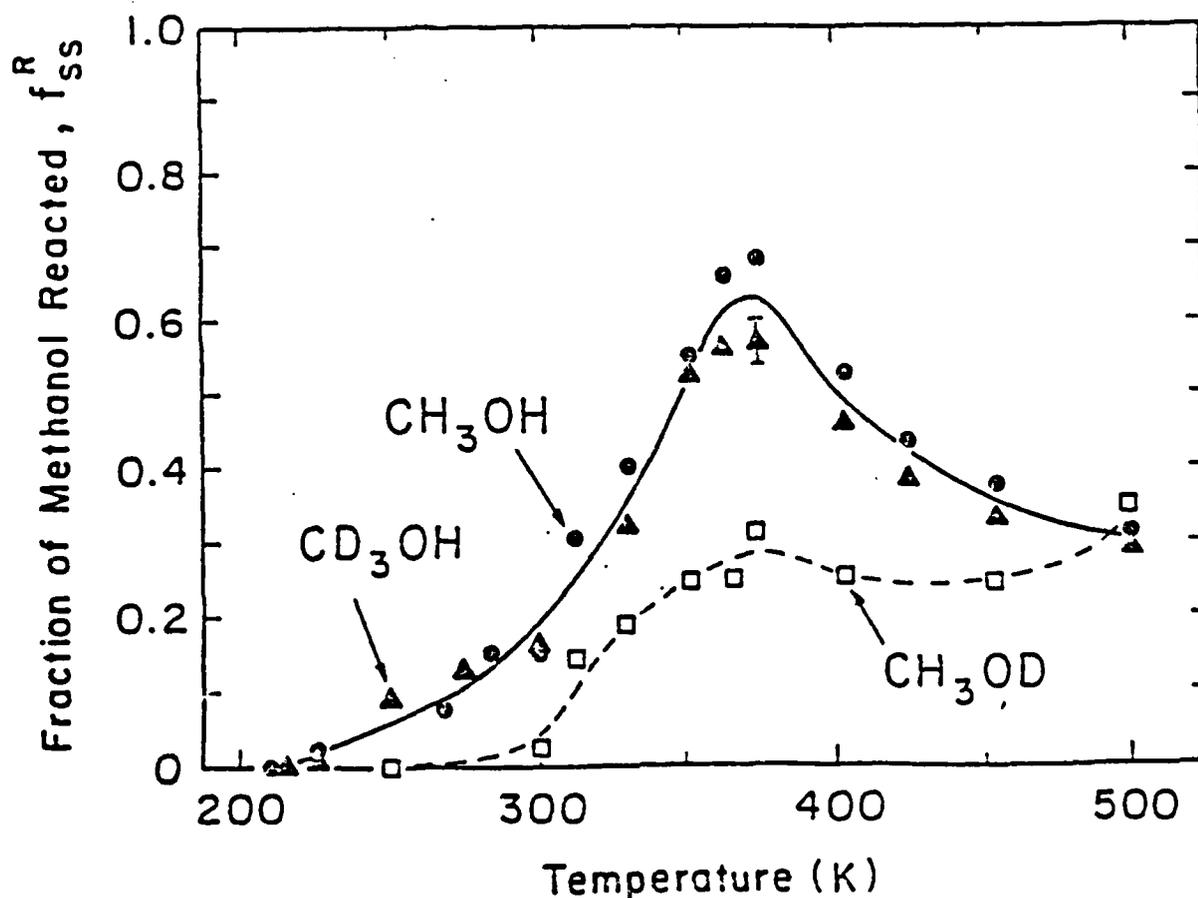
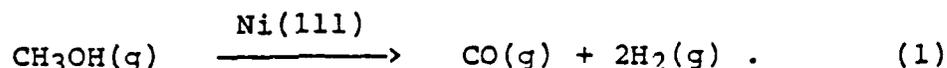


Figure 4.

One sees that these measurements, made under steady state conditions, indicate that the DKIE associated with OD-labeling is effective under steady state conditions up to 500 K in reducing the reaction rate, whereas CD₃-labeling is essentially ineffective even though C-H bonds are being broken in the overall reaction:



In Figure 4, the peaked behavior near 370 K of rate versus temperature is of interest, and a kinetic model to explain this behavior has been developed from information obtained in our studies.

The construction of the kinetic model for the complete decomposition reaction of methanol to CO(g) and H₂(g) is outlined in Figure 5, below. (Details of all measurements used to construct the model appear in reference [13]). In panel A, we have measured the steady state surface coverage, θ_{full} , of products H(ads) and CO(ads) as a function of temperature. These data permit the determination, under reaction conditions, of the fraction of open sites on the Ni(111) surface, θ_{open} , as shown in Panel B. Measurements of the reactive sticking coefficient on an empty site, S_{O}^{R} , are shown in Panel C as measured in Figure 3. The product [$S_{\text{O}}^{\text{R}} \cdot \theta_{\text{open}}$] gives the predicted overall reaction rate shown as a solid line in Panel D. The triangular points in Panel D are the experimental measurements of the overall rate of CH₃OH decomposition from (Figure 4), and are in fairly good agreement with the rate predicted from the simple function

CONSTRUCTION OF KINETIC MODEL
Methanol Decomposition on Ni(III)

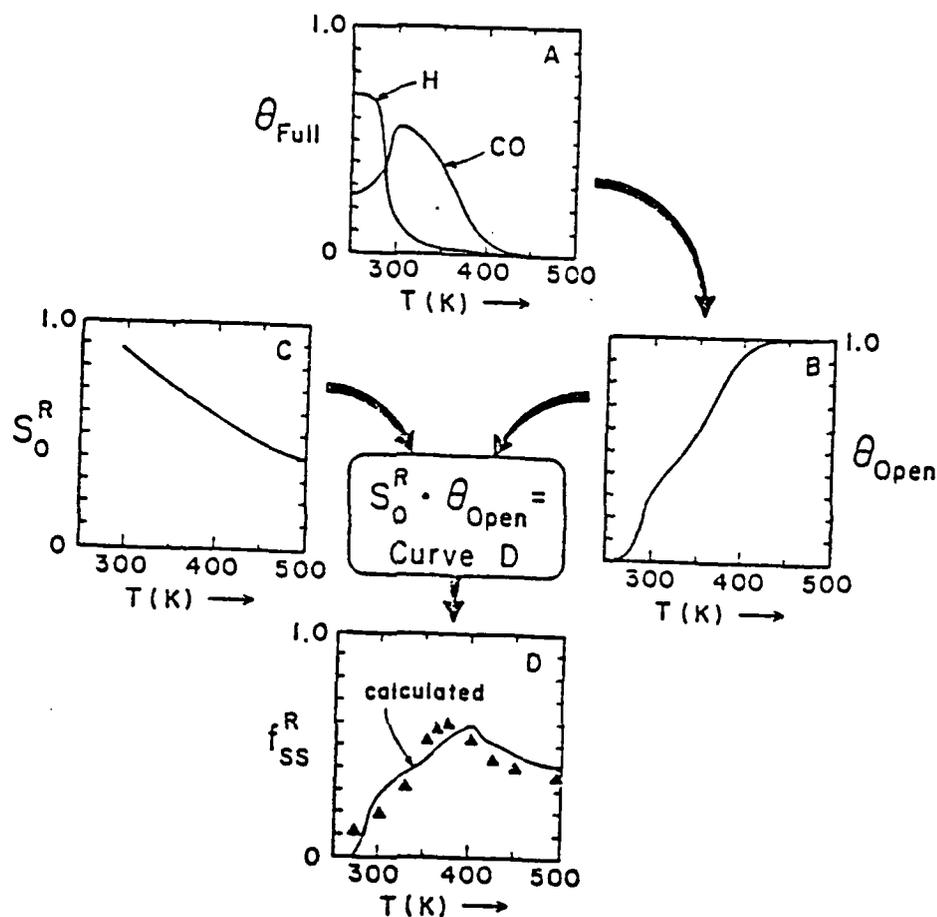


Figure 5.

$[S_O^R \cdot \theta_{open}]$. Thus, the basic functional dependence of the reaction rate for CH_3OH decomposition lives in the temperature dependence of S_O^R and of θ_{open} under reactive conditions. Further analysis of this reaction will necessarily involve understanding the kinetic and/or dynamical reasons for the decrease in S_O^R with increasing temperature.

D. Scanning Kinetic Spectroscopy (SKS) - A New Method for Evaluation of Reaction Pathways in Heterogeneous Catalysis.

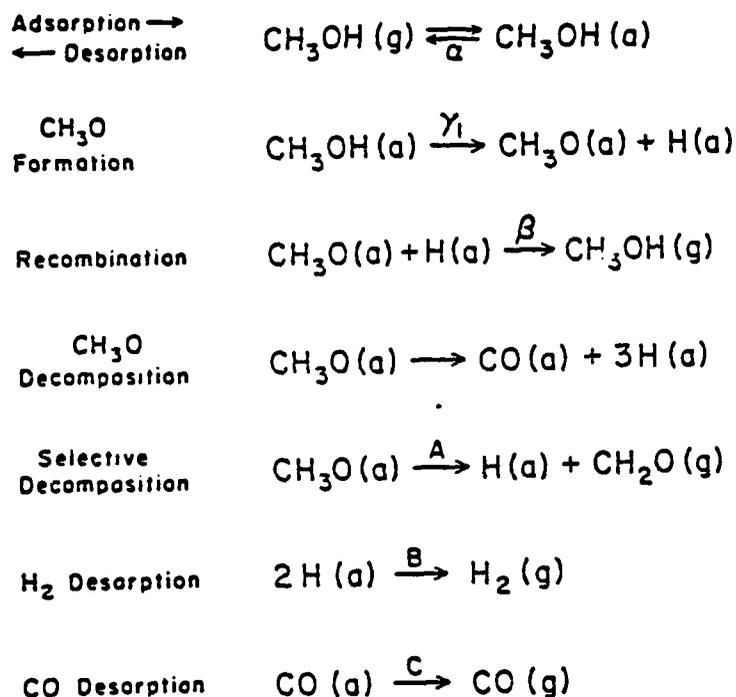
1. Expectations.

The experiments described in the previous section, and contained in references [7] and [13], involve kinetic measurements being made under isothermal conditions. Using isothermal procedures, one must repeat the measurement at various constant temperatures in order to determine the temperature dependence of the effects being measured, a time-consuming procedure.

It would be expected for a heterogeneous catalytic process involving an adsorbed molecule of some complexity (such as $\text{CH}_3\text{OH}(\text{ads})$, containing O-H, C-O, C-H and Ni-O bonds) that as the temperature of the surface is increased, various activated reaction pathways would open up at characteristic temperatures. Thus, by programming upwards the temperature of a single crystal catalyst while it interacts with a molecular beam of reactant, a characteristic fingerprint pattern of reaction channels is expected as one measures reactant consumption and product evolution simultaneously as a function of temperature. This expectation has been realized, and forms the basis for an entirely new surface technique, Scanning Kinetic Spectroscopy, SKS. A related technique, temperature programmed reaction spectroscopy (TPRS), has been widely used by others in the field [14]. It represents a limiting condition in SKS, where the flux of reactant has been reduced to zero, and where only reaction products are measured. SKS additionally measures temperature and surface coverage dependent changes in the rate of consumption of reactant, an important variable which is not measured in TPRS.

To illustrate the power of the SKS method, one "kinetic spectrogram" is shown in Figure 6. This first application of this new method has revealed an unexpected reaction channel (β), not seen in our previous measurements on this system.

ELEMENTARY PROCESSES EXPECTED IN
CH₃OH ADSORPTION AND DECOMPOSITION



SCANNING KINETIC SPECTROGRAM:
CD₃OH + Ni(111)

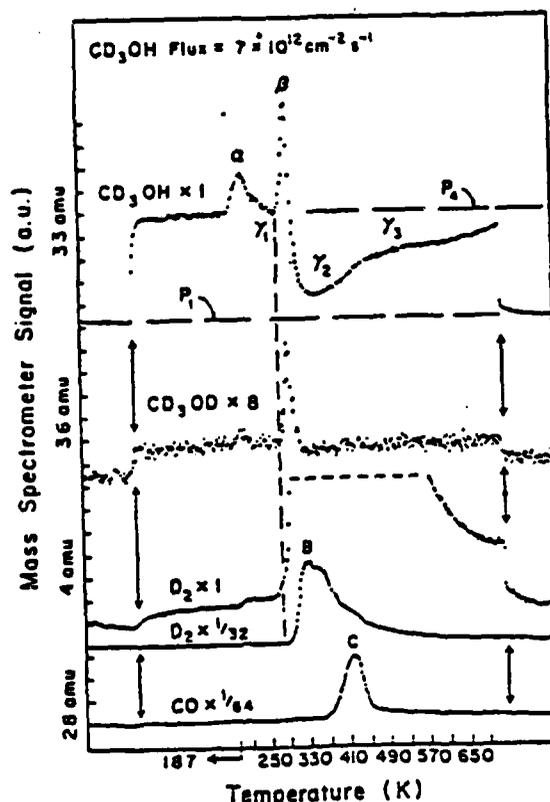


Figure 6.

2. SKS: An Example. CD₃OH + Ni(111)

In Figure 6, the Ni(111) crystal was saturated with CD₃OH at 187 K and then temperature programmed while in the CD₃OH beam. Five characteristic temperature regions of CD₃OH evolution (or consumption) are observed. These experimentally observed regions are described briefly below in Table I.

Table I

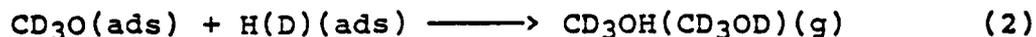
Reaction Channels for Methanol Decomposition on Ni(111)
as Observed by Scanning Kinetic Spectroscopy.

Region	Process	Description
α	$\text{CD}_3\text{OH}(\text{a}) \longrightarrow \text{CD}_3\text{OH}(\text{g})$	Desorption of intact CD_3OH
γ_1	$\text{CD}_3\text{OH}(\text{g}) \longrightarrow \text{CD}_3\text{O}(\text{a}) + \text{H}(\text{a})$	Consumption of CD_3OH as surface sites open up.*
β	$\text{CD}_3\text{O}(\text{a}) + \text{H}(\text{a}) \text{ or } \text{D}(\text{a}) \longrightarrow \text{CD}_3\text{OH}(\text{g}) \text{ or } \text{CD}_3\text{OD}(\text{g})$	Recombination of CD_3O surface intermediate, using surface H or D. The reaction is driven by D flooding of the surface due to onset of C-D bond breaking in $\text{CD}_3\text{O}(\text{a})$.
γ_2	$\text{CD}_3\text{OH}(\text{g}) + \text{site} \longrightarrow \text{products}$	Continued consumption of reactant as more surface sites open up due to hydrogen desorption.
γ_3	$\text{CD}_3\text{OH}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g}) + \text{D}_2(\text{g}) + \text{HD}(\text{g})$	Continued surface site opening as CO desorbs. Onset of steady state condition for sustained catalytic reaction.
<p>* Note: Under the particular condition of flux employed here, a negative excursion in the γ_1 region for the CD_3OH signal is not seen. In other measurements at lower flux, this negative excursion becomes very evident.</p>		

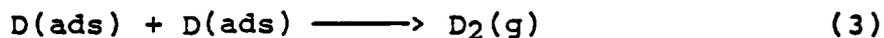
3. Hydrogen Flooding of Surface: Observation of Methoxy Recombination

The coincidence of CD_3OH and CD_3OD β peaks at about 300 K in Figure 6 identifies the β peak as due to recombination. It

is interesting to note that the β -process was completely unexpected on the basis of isothermal measurements previously made. It is also interesting to note in Figure 6 that the β -process



has its threshold at 270 K, exactly the temperature where the process



is initiated. This suggests that the presence of surface $\text{H}(\text{D})(\text{ads})$ is critically important for triggering both reaction (2) and (3) above, as would be expected. We have shown by SKS measurements that preadsorbed H atoms, or an H_2 ambient (H_2 flux ≈ 1 monolayer/second) will increase the rate of the β -recombination process.

A further observation of a DKIE on the β -recombination process is shown in Figure 7. The CH_3OH β -recombination peak occurs at 18-20 K lower temperature than the CD_3OH β -peak*. Thus, C-H(C-D) bond breaking clearly triggers the recombination event by producing enhanced surface concentration of H(a) and D(a) atoms. A model based on all of these observations has been described in greater detail [8]. The essence of this model is that hydrogen surface flooding caused by C-H or C-D bond breaking in $\text{CH}_3\text{O}(\text{ads})$ or $\text{CD}_3\text{O}(\text{ads})$ initiates the recombination process, in which unreacted methoxy species are converted to methanol which immediately desorbs.

* β - CD_3OH and CD_3OD peaks occur at identical T. (see Figure 6 and Table I).

C-H (D) BOND BREAKING ISOTOPE EFFECT
 SKS Methanol/Ni(111)

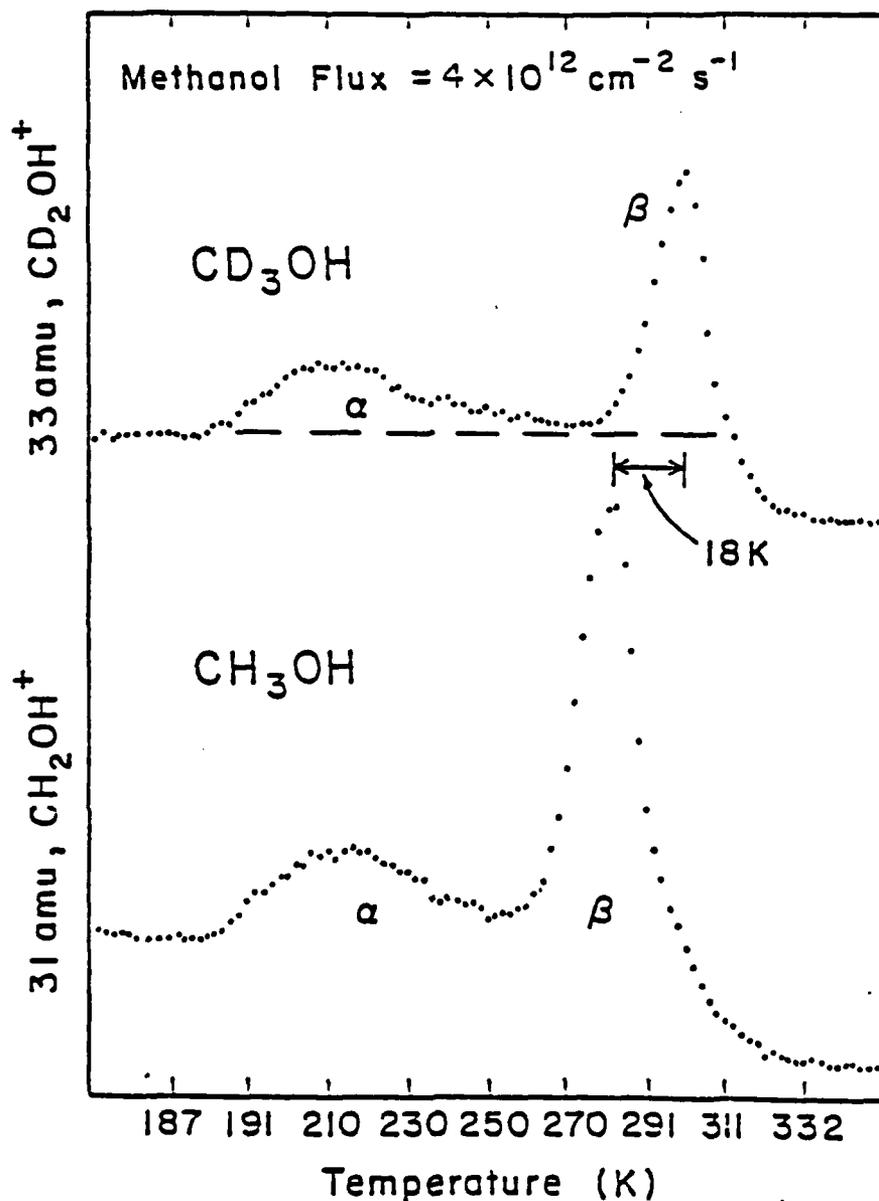


Figure 7.

4. SKS Studies of a Catalytic Promoter (Surface Modifier): $\text{CH}_3\text{OH} + \text{O}/\text{Cu}(111)$

In contrast to the work just described on Ni(111), the reaction of CH_3OH with clean Cu(111) involves only molecular

CH₃OH adsorption and molecular CH₃OH desorption. Upon adsorption of oxygen on Cu(111), several entirely new and interesting reaction pathways for CH₃OH become favorable. This is a classic example of the influence of surface modifiers (promoters) on catalytic chemistry, and forms a rich area for application of the SKS technique to survey new reaction pathways, as illustrated in Figure 8.

SCANNING KINETIC SPECTROGRAM
CD₃OH + Clean Cu(111)

SCANNING KINETIC SPECTROGRAM
CD₃OH + O/Cu(111)

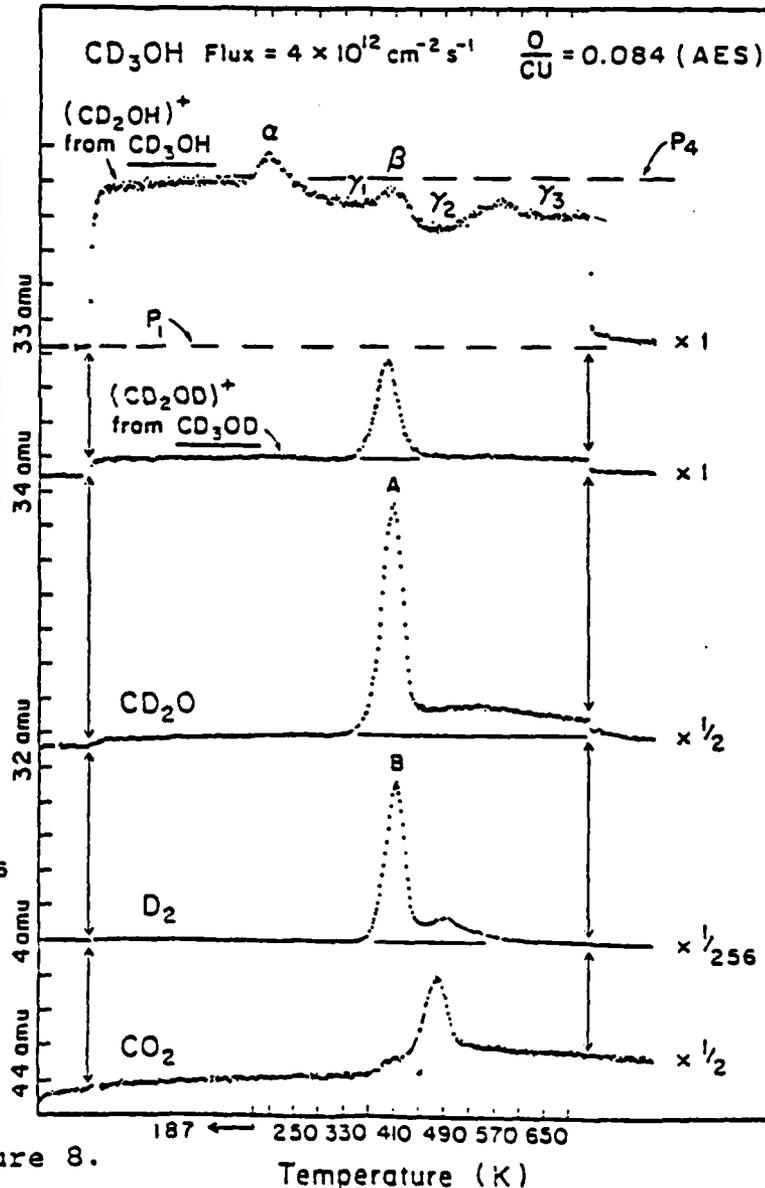
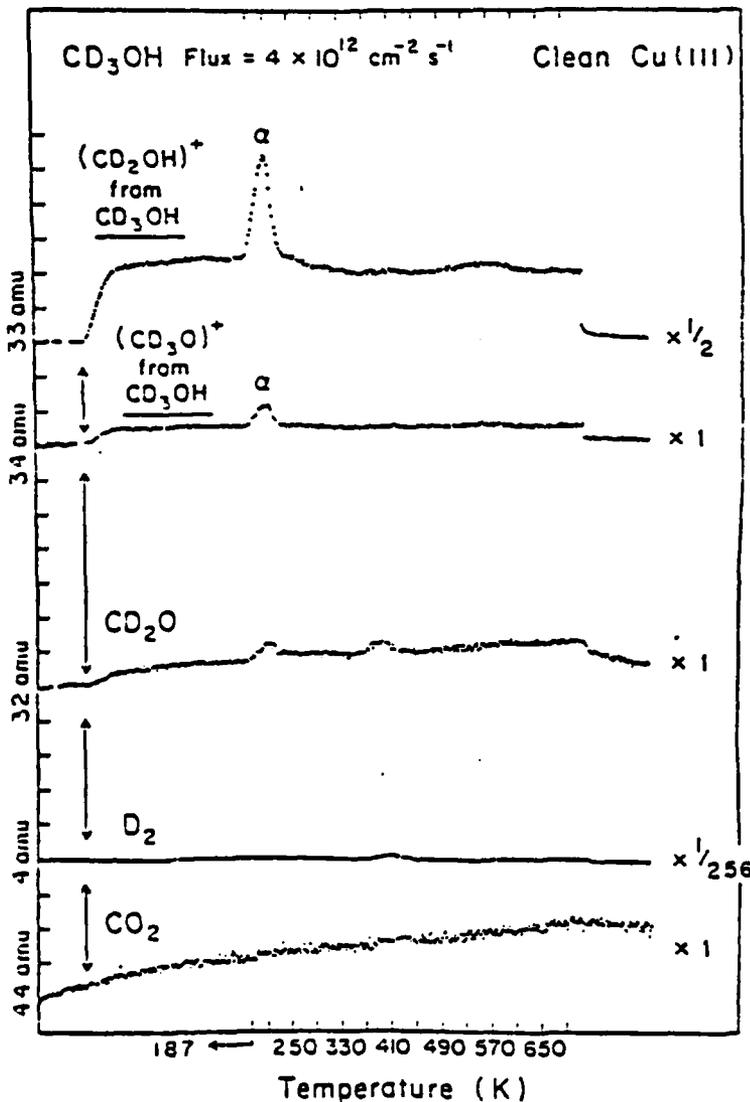


Figure 8.

The left panel on Figure 8 shows the SKS behavior of CD_3OH on $\text{Cu}(111)$. Essentially the only reaction pathway observed is the α -pathway, i.e., the desorption of the intact molecule near 225 K. Small CD_2O and D_2 features near 400 K are probably due to a tiny coverage of residual $\text{O}(\text{ads})$ observed after long Ar^+ cleaning, and annealing of the crystal [O coverage $< 2\%$ of a monolayer]. In contrast to the $\text{Cu}(111)$ surface, the SKS behavior of CD_3OH on $\text{Cu}(111) + \text{O}(\text{ads})$ [O coverage = 59% of monolayer] is rich in detail and in new decomposition products. The preadsorption of O reduces the quantity of α - CD_3OH desorption and produces a β - CD_3OH feature due to recombination of surface H with CD_3O . In addition, CD_2O and D_2 desorption channels open for the oxygenated surface, and are triggered by C-D bond breaking in $\text{CD}_3\text{O}(\text{ads})$. Finally, an intermediate $\text{CD}_x\text{O}(\text{a})$ species reacts with surface $\text{O}(\text{ads})$ to produce $\text{DCOO}(\text{a})$ which decomposes above 450 K yielding $\text{D}_2(\text{g})$ and $\text{CO}_2(\text{g})$. It is certain that the $\text{CO}_2(\text{g})$ evolution is related to C-H(D) bond breaking (probably in a formate surface complex) since the CO_2 evolution peak exhibits a DKIE as shown in Figure 9.

A number of careful studies on $\text{O}/\text{Cu}(111)$ layers of different coverages have been carried out, as well as studies involving $^{18}\text{O}(\text{ads})$ as the chemical modifier. These results are reported in a recent paper [15].

DEUTERIUM KINETIC ISOTOPE EFFECT
CARBON DIOXIDE FROM METHANOL

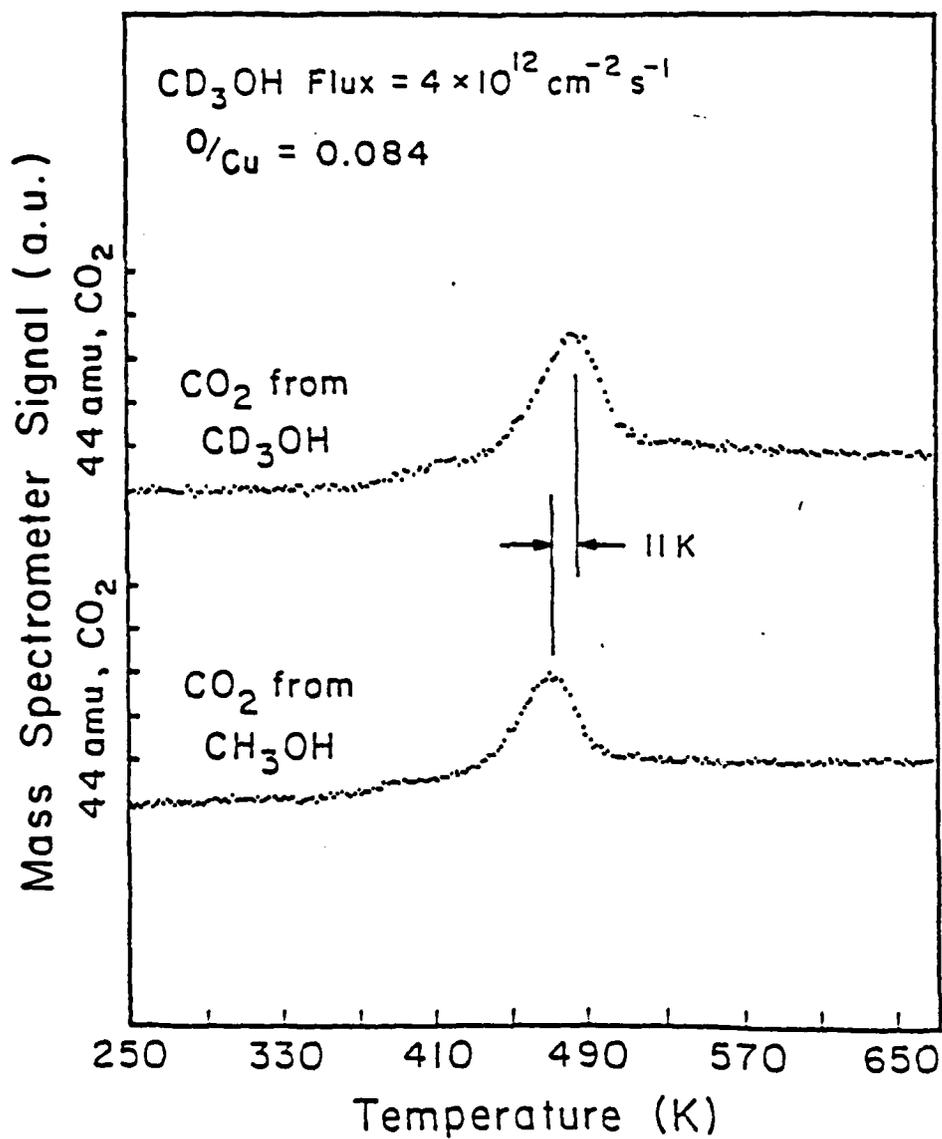


Figure 9.

We have therefore addressed a needed improvement in the measurement of the rate of thermal desorption [16].

The exceedingly high sensitivity for desorption measurements of our apparatus (Figure 1) has been employed to devise a new method for desorption kinetic analysis. Figure 10 shows the basic idea involved here. We see a typical desorption peak obtained from 0.017 monolayers of CO on Ni(111) in the top panel of Figure 10. Kinetic analysis of this peak yields the activation energy and pre-exponential factor for the desorption process, as summarized in Table II.

The first order desorption of CO is described by equation (4)

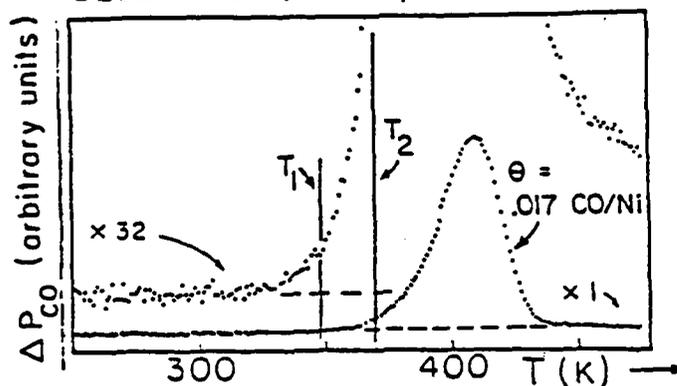
$$-\frac{dN}{dT} = \nu_d N \exp(-\Delta H_d/kT) = k_d N \quad (4)$$

where N =CO surface coverage, and ΔH_d =enthalpy of CO chemisorption. There will, however be complexities in this analysis if either ΔH_d or the pre-exponential factor ν_d , is dependent upon surface coverage N , since in general, coverage is changing significantly over the range of the desorption peak measurement.

Using the high sensitivity of our apparatus, we have expanded the threshold desorption signal by a factor of 32 as shown in Figure 10 and have performed a simple Arrhenius kinetic analysis in this initial desorption region at about 350-370 K [17]. This measurement is made over a temperature range where surface coverage has changed only by about 0.0003 monolayers, i.e., under an essentially constant coverage condition! The expanded sensitivity data yield an activation energy of 27.1 Kcal/mole and a

This measurement is made over a temperature range where surface coverage has changed only by about 0.0003 monolayers, i.e., under an essentially constant coverage condition! The expanded sensitivity data yield an activation energy of 27.1 Kcal/mole and a pre-exponential factor of $1 \times 10^{14} \text{ sec}^{-1}$. These kinetic parameters agree very favorably with the data shown in Table II, measured by more conventional methods.

THRESHOLD TEMPERATURE PROGRAMMED
DESORPTION (TTPD), CO + Ni (III)



THRESHOLD ARRHENIUS PLOT - TTPD
CO + Ni (III)

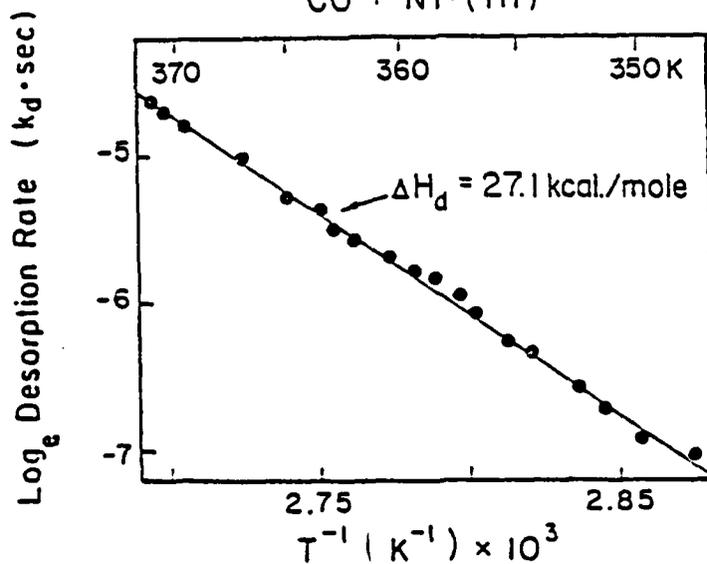


Figure 10.

Table II
Comparison of Desorption Kinetic Parameters
for CO/Ni(111).

Method	v_d (sec^{-1})	ΔH_d Kcal/mole
Threshold Desorption ($\Delta\theta = 0.0003$)	1×10^{14}	27.1

Full Desorption These Data ($\Delta\theta = 0.0167$)	4×10^{14}	28.3

Isosteric Heat of adsorption (ref. 18) ($\theta \approx 0.1$)	---	26.5 ± 1.1

Crude Kinetic Fit (ref. 19;20) These Data	10^{14} (assumed value)	27.1

The good agreement of the TPPD method with other conventional methods gives us confidence that the TPPD method will be of high accuracy in the measurement of thermal desorption kinetics from surfaces, having particular applicability where significant coverage dependence of ΔH_d and v_d occur. The advantages of the TPPD method for studying desorption in a systematic manner as a function of coverage are listed below:

- Desorption kinetics are measured at essentially constant coverage, avoiding coverage dependent changes in kinetic parameters during a particular measurement.
- Wide dynamic range for adsorbate fractional coverages from about 0.005 monolayer to 1 monolayer. The method may be applied accurately in a wide range of initial surface coverages, probing coverage effects on kinetic details.
- Simplicity of analysis.
- Dense array of digital data points.

III. Summary of Results - Functional Group Chemistry on Metal or Chemically-Modified Metal Surfaces.

A. Summary of New Technique Development.

The work carried out to date has been directed at developing swift and efficient survey methods for the study of chemical kinetics in surface reactions. The following experimental methods have been developed and explored in model systems as listed below:

- Measurement of a Reactive Sticking Coefficient in the Limit of Zero Surface Coverage, S_0^R .

Here a kinetic method has been developed to measure a fundamental rate under molecular beam gas density conditions - namely the efficiency of molecular decomposition on a clean single crystal surface. While the sticking coefficient is not an average over all incoming and outgoing reactant trajectories, it may be used quite satisfactorily in differential rate measurements for isotopically labeled species.

- Use of Deuterium Kinetic Isotope Effect in Picking out the Rate Controlling Step in a Catalytic Reaction at Steady State Condition.
- Scanning Kinetic Spectroscopy - A Rapid Survey Technique Probing the Opening of Reaction Channels in Surface Chemistry.
- Threshold Temperature Programmed Desorption - A Simple High Sensitivity Method for Kinetic Studies of Desorption at Constant Surface Coverage.

B. Summary of Some Scientific Ideas Derived from this Work.

In addition to determining the basic reaction characteristics for several specific systems [$\text{CH}_3\text{OH} + \text{Ni}(111)$];

CH₃OH+Cu(111); CH₃OH+O/Cu(111)], several general scientific concepts have been discovered or reaffirmed as listed below:

- The thermal separability of certain reaction channels as evidenced by sharp, correlated uptake and desorption features in SKS measurements.
- The role of surface site opening by adsorbed product desorption in enhancing the rate of a catalytic decomposition process.
- The significant role of surface hydrogen in controlling specific dehydrogenation or hydrogenation elementary processes on a catalytic surface.
- The role of surface modifiers on generating new reaction pathways for molecular dissociation to new products.

IV. Publications Resulting From This Work - 1983-85.

The following papers have been published or submitted as a result of ARO support in our first contract period.

1. "Observation of a Deuterium Kinetic Isotope Effect in the Chemisorption and Reaction of Methanol on Ni(111)", SURFACE SCIENCE 146, 199 (1984).
2. S. M. Gates, J. N. Russell, Jr., and J. T. Yates, Jr., "Reaction Kinetic Measurements on Single Crystal Catalysts: Methanol Decomposition on Ni(111)", J. CATALYSIS 92, 25-34 (1985).
3. S. M. Gates, J. N. Russell, Jr. and J. T. Yates, Jr., "Summary Abstract: Scanning Kinetic Spectroscopy (SKS), A Rapid Probe of Surface Reaction Processes," accepted, J. VAC. SCI. TECHNOL A 3(3), 1472 (1985).
4. S. M. Gates, J. N. Russell, Jr., and J. T. Yates, Jr., "Scanning Kinetic Spectroscopy (SKS): A New Method for Investigation of Surface Reaction Processes, SURFACE SCIENCE, 159, 233 (1985).

5. J. N. Russell, Jr., S. M. Gates, and J. T. Yates, Jr., "Reaction of Methanol with Cu(111) and Cu(111) + O(ads)", accepted, SURFACE SCIENCE.
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