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Publication Date

1976-04-01

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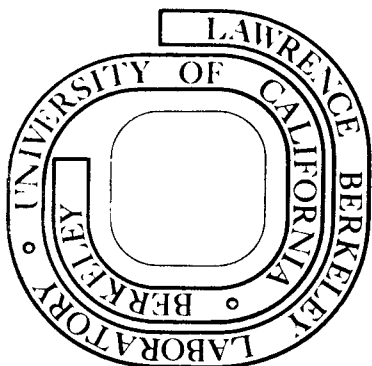
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April 16, 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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Limitations of Kinetic Studies of Catalytic Reactions on a Single Crystal
Surface at Low Pressures in an Ultra-High Vacuum System

by

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ABSTRACT

We present an analysis of the kinetics of catalytic reactions occurring on a small area ($\sim 1 \text{ cm}^2$), single-crystal surface in an ultra-high vacuum system at low pressures (10^{-8} - 10^{-4} Torr). We find that one can measure reaction probabilities as low as 10^{-4} under flow conditions and 10^{-7} under batch conditions. For the purpose of illustration we give two practical examples: hydrogenolysis of isobutane and dehydrogenation of cyclohexene on platinum surfaces.

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INTRODUCTION

Investigations into the chemical and physical basis of heterogeneous catalysis are being pursued at present along two different lines. On the one hand, studies of real catalysts have produced a great deal of empirical evidence on how to prepare surfaces with specific desired properties to carry out a large number of catalytic reactions and on the kinetics of these reactions [1,2]. Such studies can be utilized directly in industrial applications because of the similarity of the experimental conditions employed. A major drawback is that real catalysts can be characterized only incompletely on an atomic scale. On the other hand, studies in ultra-high vacuum are being performed on surfaces that are well characterized as to their geometrical structure and composition by a variety of surface-sensitive experimental techniques [3,4]. From the point-of-view of catalysis, these ultra-high vacuum studies have the drawback of being concerned with simple systems under conditions rather removed from those used in industrial applications. In an effort to bridge the gap between these two approaches Somorjai and coworkers [5-8] have demonstrated recently that it is possible to study reactions of catalytic interest on well-characterized single-crystal surfaces. This work has shed considerable light on the principles underlying the unique properties of certain materials as catalysts.

In this paper, we examine the conditions under which it is feasible to study catalytic reactions in a typical ultra-high vacuum system on a single-crystal surface, i.e. with a catalytically active surface area of about 1 cm^2 . Specifically, we look at a simple reaction mechanism and its kinetics in order to arrive at estimates of measurable reaction probabilities under

batch or flow conditions at low pressures (10^{-4} - 10^{-8} Torr). We then illustrate these considerations by analyzing data on two sample reactions: hydrogenolysis of isobutane and dehydrogenation of cyclohexene on platinum surfaces.

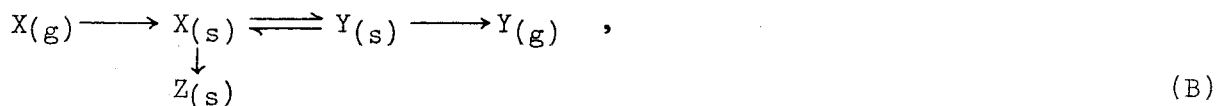
THEORETICAL ANALYSIS

We wish to consider a simple reaction mechanism which can be depicted schematically as follows:



Reactant molecules X in the gas phase adsorb onto the catalyst surface at a rate which is proportional to the sticking probability $s(\theta_X)$ (vs. coverage θ_X), and a fraction x of these adsorbing molecules is converted into product molecules Y which desorb back into the gas phase. The quantity $xs(\theta_X)$ can thus be interpreted as the overall reaction probability r. The mechanism (A) adequately describes many catalytic reactions at low pressure, including the ones of interest to us, since it is found experimentally that at low pressure the initial rate of reaction is proportional to reactant partial pressure and desorption of the product is not rate-limiting [7-10].

Furthermore, the mechanism (A) is a condensed version of the following fairly general mechanism



where $Z(s)$ is a poison, since the rate equations derived from (B), assuming a steady-state for θ_X and θ_Y , reduce to the rate equations derived from (A).

(The hydrocarbon reactions we are interested in usually occur in excess hydrogen so that the mechanisms (A) and (B) only describe the dependence of the kinetics on the reactant hydrocarbon.)

The balance for the number of molecules of species i in the system volume can be written as follows:

$$\frac{V}{k_B T_g} \frac{dp_i}{dt} = L_i - \frac{S_i p_i}{k_B T_g} + a(r_{di} - r_{ai}) \quad (1)$$

with the following definitions of symbols:

| | |
|---|---|
| V : system volume (cm^3) | S_i : pumping speed ($\text{cm}^3 \text{sec}^{-1}$) |
| k_B : Boltzmann constant | a : surface area of crystal (cm^2) |
| T_g : gas temperature | r_{di} : desorption rate ($\text{sec}^{-1} \text{cm}^{-2}$) |
| L_i : leak rate (sec^{-1}) | r_{ai} : adsorption rate ($\text{sec}^{-1} \text{cm}^{-2}$) |
| p_i : partial pressure (dynes cm^{-2}) | |

Let $i = 1$ for the reactant and $i = 2$ for the product. In the following we shall analyze the rate Eq.(1) for the cases of static and flow conditions separately.

(1) Batch reactor

In this case $L_i = S_i = 0$ for $i = 1, 2$. For the sake of simplicity, we also assume desorption of reactants and readsorption of products to be negligible, i.e. $r_{d1} = r_{a2} = 0$. Equation (1) then reduces to

$$n_1 \frac{dp_1}{dt} = -A_1 p_1 s(\theta_1) \quad (2a)$$

$$n_2 \frac{dp_2}{dt} = x A_1 p_1 s(\theta_1). \quad (2b)$$

With the abbreviations $n_1 = V/k_B T_g$ and $A_1 = a(2\pi m_1 k_B T_g)^{-\frac{1}{2}}$. In addition,

one has an equation for θ_1 as a function of t :

$$n_2 \frac{d\theta_1}{dt} = A_1 p_1 s(\theta_1), \quad (3)$$

where we set $n_2 = aN_0$ with N_0 being the number of adsorption sites per unit area. Equations (2a,b) and (3) are nonlinear because of $s(\theta_1)$. However, under appropriate experimental conditions, p_1 will not change too much so that Eqs.(2a,b) and (3) can be linearized. For the sake of simplicity we assume simple Langmuir kinetics for adsorption of the reactant. Then from Eq.(3)

$$\theta_1(t) = 1 - \exp(-t/\tau) \quad , \quad (4)$$

with $\tau = n_2/A_1 p_{10} s_{10}$ and $p_{10} = p_1(t=0)$. Inserting Eq.(4) into Eq.(2a) one arrives at

$$p_1(t) = p_{10} \exp(\alpha\tau[\exp(-t/\tau) - 1]), \quad (5)$$

with $\alpha = A_1 s_{10}/n_1$. If p_1 does not change much, as assumed, then $\alpha\tau \ll 1$ so that

$$p_1(t) = p_{10} - \frac{n_2}{n_1} [1 - \exp(-t/\tau)] \quad . \quad (6)$$

Typically, $V = 10^4 \text{ cm}^3$, $a = 1 \text{ cm}^2$, and $N_0 = 10^{15} \text{ cm}^{-2}$, so that

$p_1(0) - p_1(\infty) = n_2/n_1 = 3 \times 10^{-6} \text{ Torr}$. Hence, our assumptions are consistent if the reactant pressure p_{10} is approximately $3 \times 10^{-5} \text{ Torr}$ or larger. As we shall see, this is indeed the case in a typical batch reaction.

Solving Eq.(2b), using Eq.(6), one finds for the product pressure

$p_2(t)$

$$p_2(t) = p_2(0) + x \frac{n_2}{n_1} [1 - \exp(-t/\tau)] \quad . \quad (7)$$

The reaction probability r , defined previously as $r = x s_{10}$, can thus be determined in two ways. From Eqs.(6) and (7)

$$r = s_{10} \frac{p_2(\infty) - p_2(0)}{p_1(0) - p_1(\infty)} \quad . \quad (8)$$

This requires knowledge of the initial sticking coefficient s_{10} , and it may be difficult to measure accurately the small change in reactant pressure $p_1(0) - p_1(\infty)$. Equivalently, from Eq.(7)

$$r = \frac{n_1}{p_1(0)A_1} \frac{dp_2(t=0)}{dt} \quad (9)$$

This second method involves a determination of the slope of the curve $p_2(t)$ at $t = 0$, but one does not have to know the sticking coefficient s_{10} . On the other hand, by combining the two methods one would be able to determine both r and s_{10} .

In order to arrive at an estimate of the lowest reaction probability measurable by the batch method, we choose to focus on Eq.(8) although Eq.(9) would of course lead to the same result. As mentioned earlier, $p_1(0) - p_1(\infty)$ is on the order of 10^{-6} Torr. In addition, one can expect to be able to measure a change in p_2 of 10^{-10} Torr under favorable circumstances. Furthermore, experimental constraints (interference by background gases) put a lower limit of about 10^{-3} on the value of s_{10} , corresponding to a reaction time of about 100 seconds at 10^{-5} Torr of reactant partial pressure. Hence, we find a lower bound of about 10^{-7} for a measurable reaction probability although 10^{-6} may be a more realistic value.

(2) Flow reactor

In analogy to Eq.(2) we have in this case

$$n_1 \frac{dp_1}{dt} = L_1 - B_1 p_1 - A_1 p_1 s(\theta_1) \quad (10a)$$

$$n_1 \frac{dp_2}{dt} = -B_2 p_2 + x A_1 p_1 s(\theta_1) \quad (10b)$$

with $B_i = S_i/kTg$. If the leaking and pumping rates for the reactant are much faster than the rate of adsorption, then p_1 is constant and equal to

L_1/B_1 . Hence, $\theta_1(t) = 1 - \exp(-t/\tau)$ as in the case of the batch reactor.

Equation (10b) can thus be rewritten as

$$n_1 \frac{dp_2}{dt} = -B_2 p_2 + x_{A_1} p_1 s_{10} \exp(-t/\tau) . \quad (11)$$

The solution for Eq.(11) is

$$p_2(t) = \frac{\gamma}{\beta - 1/\tau} [\exp(-t/\tau) - \exp(-\beta t)] , \quad (12)$$

with $\beta = B_2/n_1$ and $\gamma = x_{A_1} p_1 s_{10}/n_1$. Note that $A_1/B_2 = \frac{1}{4} \bar{v}_1 a/S_2$, where \bar{v}_1

is the average speed of the reactant molecules, and $\beta\tau = n_2 B_2/n_1 p_1 A_1 s_{10}$.

In a typical flow experiment $S_2 \approx 10^3 \text{ cm}^3 \text{ sec}^{-1}$ and $p_1 \approx 3 \times 10^{-8} \text{ Torr}$. This

implies that $A_1/B_2 \approx 10$ and, in turn, $\beta\tau \gg 1$. Therefore, Eq.(12) can be

simplified as follows:

$$p_2(t) = x_{s_{10}} p_1 \frac{A_1}{B_2} \exp(-t/\tau) . \quad (13)$$

For the reaction probability $r = x_{s_{10}}$ we obtain from Eq.(13)

$$r = p_2(0) B_2 / p_1 A_1 . \quad (14)$$

The advantage of the flow method over the batch method is that the continuous pumping reduces interference by background gases. However, this is achieved at the cost of lower sensitivity. One can attain a workable compromise by reducing the high pumping speed (~ 100 liters/sec) typical for an ion-pumped ultra-high vacuum system down to about 1 liter/sec, using a gate valve. At this pumping speed the highest practicable reactant pressure is $\sim 10^{-6}$ Torr. (A higher pressure would tend to overload the pump.) Thus, we conclude from Eq.(14) that reaction probabilities as low as 10^{-4} can be measured under flow conditions.

PRACTICAL EXAMPLES

We wish to describe first some general features of the experimental set-up which was used in performing the reactions to be discussed below. The experiments were carried out in UHV systems pumped by ion pumps and equipped with LEED/Auger facilities. Total pressures were monitored by a nude ionization gauge and partial pressures by a quadrupole mass spectrometer calibrated by the ion gauge [11]. (The base pressure was typically 2×10^{-9} Torr after bake-out.) Before each experimental run, the catalyst surface was cleaned using standard procedures such that an Auger spectrum revealed no impurities [7,8]. If the catalyst was a single-crystal surface, its ordered surface structure was ascertained by low-energy electron diffraction. The crystal could be heated ohmically. The crystal temperature was determined either by a thermocouple spot-welded to the crystal or by an infrared pyrometer. The reactant gases were admitted to the system through a variable-leak valve. In dry runs the measured catalytic activity was established to be due to the crystal and not due to its support, the walls of the system, or the hot mass spectrometer filament.

We now proceed to examine data on two catalytic reactions in terms of our theoretical analysis.

(1) Hydrogenolysis of isobutane (batch conditions)

This reaction has been investigated by Hagen and Somorjai [8] as part of a study of the effect of Au on the catalytic activity of Pt and Ir. We consider here their data for the case where the catalyst was a piece of polycrystalline Pt foil with an active area of 1.5 cm^2 . The system volume was 15 liters. After the crystal had been cleaned, a hydrogen-hydrocarbon

mixture in the ratio of 5:1 was admitted to the system such that the partial pressure of the hydrocarbon was 5×10^{-5} Torr. The reaction was initiated by raising the sample temperature to 300°C . The only hydrogenolysis product observed was methane. Figure 1 shows the production of methane as a function of time, with $t = 0$ marking the start of the reaction. From the curve in Fig. 1 one obtains an initial reaction rate $dp_2(t=0)/dt$ of 2.7×10^{-7} Torr/min. This yields, using Eq.(9), a value of 1.1×10^{-4} for the reaction probability r .

In addition, we can also make an estimate of the initial sticking probability s_{10} for isobutane, using the above value for r in Eq.(8), although the change in reactant partial pressure was not measured. As pointed out in Section 2, $p_1(0) - p_1(\infty)$, being determined by the number of active sites on the catalyst surface and the system volume, is of the order of 3×10^{-6} Torr. On the other hand, Fig. 1 indicates that $p_2(\infty) - p_2(0) \approx 3 \times 10^{-7}$ Torr. Hence, it follows from Eq.(8) that $s_{10} \approx 10^{-3}$. The above figures for r and s_{10} may be interpreted as showing that under the conditions given, the hydrogenolysis of isobutane on Pt is adsorption-limited, i.e. a reactant molecule, once it is adsorbed, has a substantial chance of being converted into a product molecule (cf. Table I).

We also note that the lowest reaction probability which could be measured reliably by Hagen and Somorjai [8] was of the order of 10^{-7} for dehydrocyclization of n-heptane to toluene on an Ir/Au surface. This is in agreement with our theoretical analysis.

(2) Dehydrogenation of cyclohexene (flow conditions)

In our second example we present data on the dehydrogenation of cyclohexene to benzene on a Pt(S)-[6(111)×(100)] surface. (This surface consists of

six-atom-wide terraces of (111) orientation and one-atom-high steps of (100) orientation, as verified by low-energy electron diffraction. Its Miller Index designation is (755).) The dehydrogenation of cyclohexene occurs readily on a number of Pt surfaces since at low hydrogen pressure the reaction product is strongly favored by thermodynamic equilibrium [12]. This has enabled Blakely and Somorjai [7] to study in considerable detail to what extent the dehydrogenation as well as the hydrogenolysis of cyclohexene and cyclohexane are structure-sensitive.

The system volume was again 15 liters, and the catalyst had an active area of 1 cm^2 . After the crystal had been cleaned, it was allowed to cool to the reaction temperature. The desired hydrogen/cyclohexene mixture was then admitted to the system, and the production of benzene was monitored as a function of time. Figure 2 shows two typical curves for the temporal evolution of benzene. The reaction rate is quite high and can be observed easily, but the crystal poisons rather rapidly. At low reactant pressure one can observe the reaction rate reach a maximum, whereas at higher reactant pressure this maximum cannot be resolved experimentally. (Auger and LEED measurements show that at the end of a reaction the crystal is covered with about one monolayer of disordered carbon.)

During all experimental runs the measured pump-out time for the hydrocarbons was 34 sec. With a system volume of 15 liters, this implies a pumping speed S_2 of $450 \text{ cm}^3 \text{ sec}^{-1}$. Thus, A_1/B_2 in Eq.(12) takes a value of 14. Furthermore, since $p_1 \sim 3 \times 10^{-8}$ Torr (cf. Fig. 2) and $s_{10} \sim 0.1$ (see below), one finds that in Eq.(12) $\beta\tau \approx 40$ so that Eq.(13) is a good approximation to Eq.(12). From Eq.(14) it then follows that the initial reaction probability r is equal to $p_{\text{max}}(\text{benzene})$ divided by 14 times $p(\text{cyclohexene})$. In Fig. 3

we show some results for the dependence of the reaction probability on the surface temperature and on the hydrogen/cyclohexene ratio. Note that the reaction probability increases with increasing hydrogen/cyclohexene ratio and decreases with increasing surface temperature. Both these trends are contrary to what one would expect from equilibrium considerations [12].

Curves such as those displayed in Fig. 2 also show that at a reactant partial pressure of $\sim 3 \times 10^{-8}$ Torr it takes about 10 minutes for the crystal to become catalytically inactive. (As mentioned above, this poisoning is due to the growth of a disordered carbonaceous layer on the surface.) But an exposure of ~ 20 Langmuir to cover the surface with a monolayer implies that the initial sticking coefficient s_{10} for cyclohexene is of the order of 0.1. Comparing this figure with the measured reaction probabilities, we find that the probability for an adsorbed reactant molecule to be converted to a product molecule is of order 1. Hence, we can say that under the conditions given, the dehydrogenation of cyclohexene on a Pt(S)-[6(111) \times (100)] surface is adsorption-limited (cf. Table I).

CONCLUDING REMARKS

We have shown that it is possible to investigate reactions of catalytic interest on a single-crystal surface in a typical ultra-high vacuum system. Our simple theoretical analysis indicates, in agreement with experiments, that one can measure reaction probabilities as low as $\sim 10^{-4}$ under flow conditions and $\sim 10^{-7}$ under batch conditions. These figures should be representative for the experimental conditions in question, although they might be improved somewhat, e.g. by using a pump which can handle higher pressures than an ion pump or by designing the reactor as small as possible. Clearly, many more

catalytic reactions of different types should be amenable to study along the lines described here. Furthermore, a more comprehensive analysis of data such as those given in Fig. 3 may be expected to yield a great deal of interesting kinetic information on such reactions.

Acknowledgments:

This work was supported by the U. S. Energy Research and Development Administration and the Office of Naval Research, Grant N00014-75-C-0890.

References

- (1) M. Boudart, in Physical Chemistry: An Advanced Treatise, Vol. VII, edited by H. Eyring (Academic Press, New York, 1975), p. 350.
- (2) J. H. Sinfelt, Progr. Solid State Chem., 10, 55 (1975).
- (3) See several articles in Interactions on Metal Surfaces, edited by R. Gomer (Springer, New York, 1975).
- (4) See papers presented at 1974 American Vacuum Society Meeting, as published in J. Vac. Sci. Technol., 12, No. 1 (1975).
- (5) D. Kahn, E. E. Petersen, and G. A. Somorjai, J. Catal., 34, 294 (1974).
- (6) J. L. Gländ, K. Baron, and G. A. Somorjai, J. Catal., 36, 305 (1975).
- (7) D. W. Blakely and G. A. Somorjai, J. Catal. (to be published).
- (8) D. I. Hagen and G. A. Somorjai, J. Catal., 41, 466-481 (1976).
- (9) D. W. Blakely, private communication.
- (10) D. I. Hagen, private communication.
- (11) No attempt was made to correct for the ion gauge sensitivity varying between different gases, although this could be done using data by F. Nakao, Vacuum, 25, 431 (1975).
- (12) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley and Sons, New York, 1969).

Table I
Estimated Reaction-, Conversion-, and Sticking Probabilities for
Two Hydrocarbon Reactions at Low Pressures

| Reaction | Catalyst | Initial Sticking Probability for Reactant (s_{10}) | Conversion Probability (x) | Reaction Probability ($r=xs_{10}$) |
|---|-------------------------|--|--------------------------------|--------------------------------------|
| hydrogenolysis of isobutane to methane | polycrystalline Pt foil | $\sim 10^{-3}$ | ~ 0.1 | $\sim 10^{-4}$ |
| dehydrogenation of cyclohexene to benzene | Pt(S)-[6(111)×(100)] | ~ 0.1 | ~ 1 | ~ 0.1 |

Figure Captions

Fig. 1. Hydrogenolysis of isobutane on a polycrystalline Pt surface under batch conditions: production of methane as a function of time.

The reaction temperature of the catalyst is 300°C.

$p(\text{iso-C}_4\text{H}_{10}) = 5 \times 10^{-5}$ Torr, $p(\text{H}_2)/p(\text{iso-C}_4\text{H}_{10}) = 5$.

Fig. 2. Dehydrogenation of cyclohexene on a Pt(S)-[6(111)×(100)] surface under flow conditions: production of benzene as a function of

time. The reaction temperature of the catalyst is 150°C.

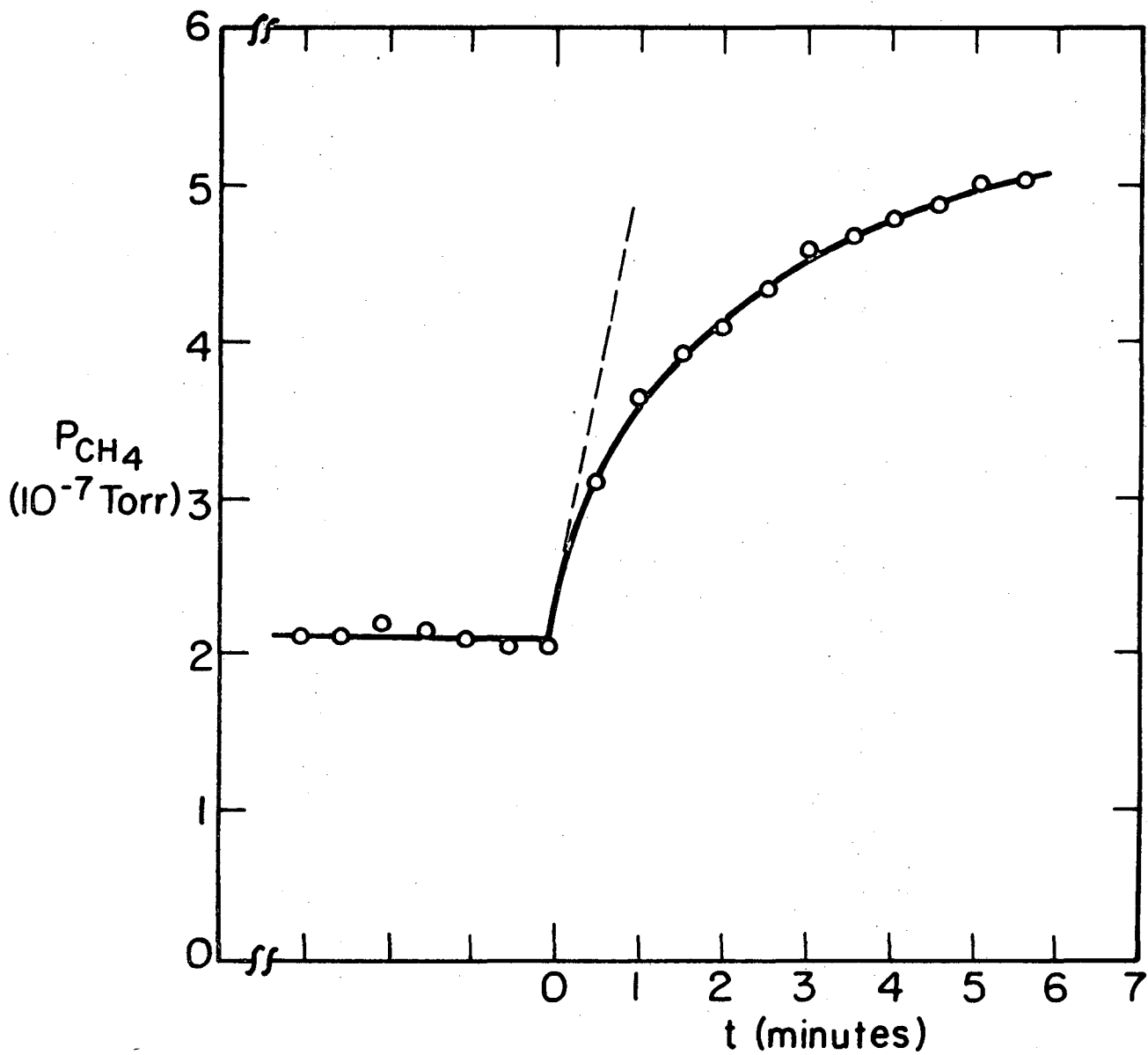
o: $p(\text{C}_6\text{H}_{10}) = 1.1 \times 10^{-8}$ Torr, $p(\text{H}_2)/p(\text{C}_6\text{H}_{10}) = 60$;

Δ: $p(\text{C}_6\text{H}_{10}) = 7.8 \times 10^{-8}$ Torr, $p(\text{H}_2)/p(\text{C}_6\text{H}_{10}) = 5.5$.

Fig. 3. Reaction probabilities for the dehydrogenation of cyclohexene to benzene on a Pt(S)-[6(111)×(100)] surface.

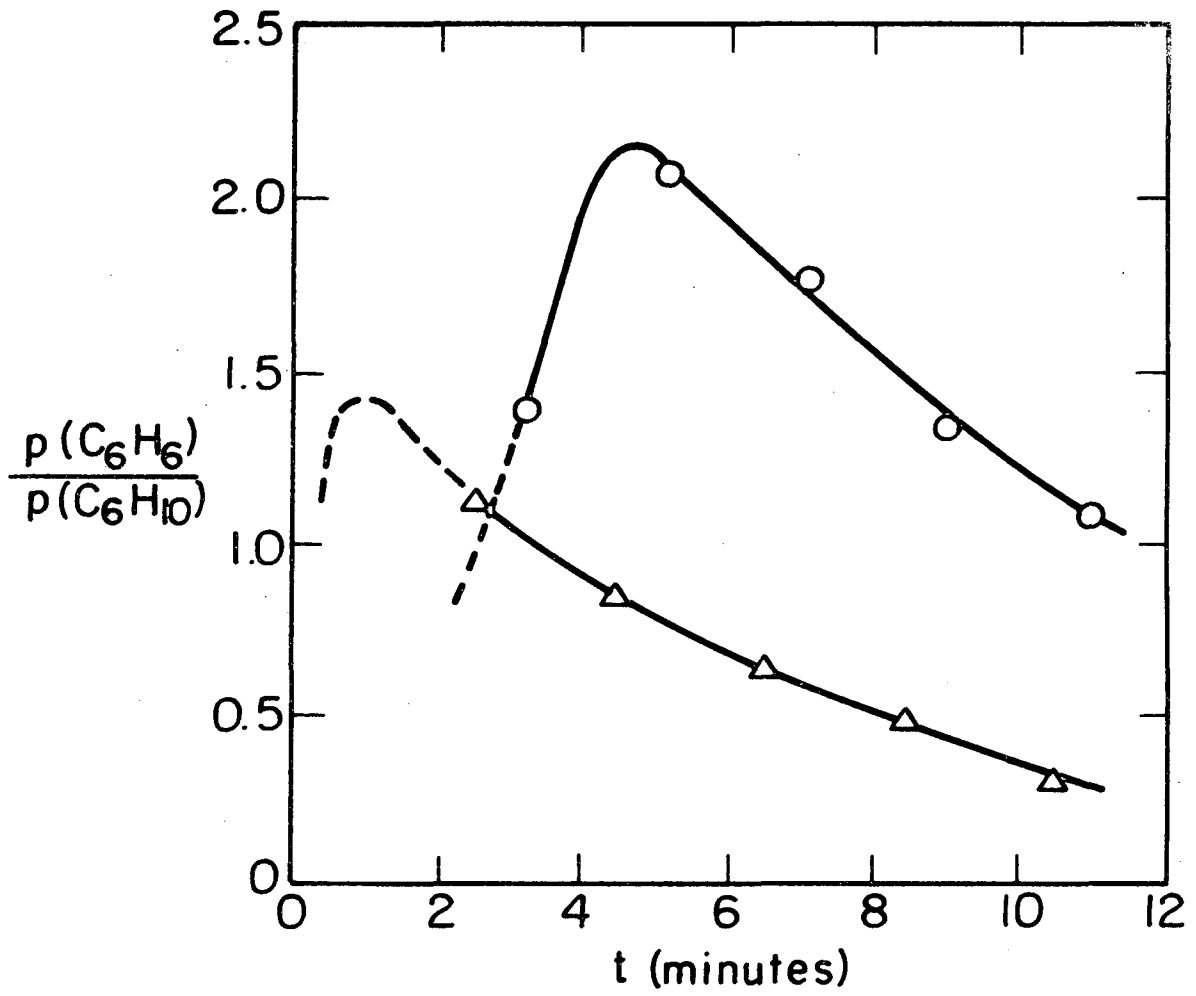
▲: surface temperature $T_s = 20^\circ\text{C}$, o: $T_s = 150^\circ\text{C}$,

x: $T_s = 300^\circ\text{C}$.



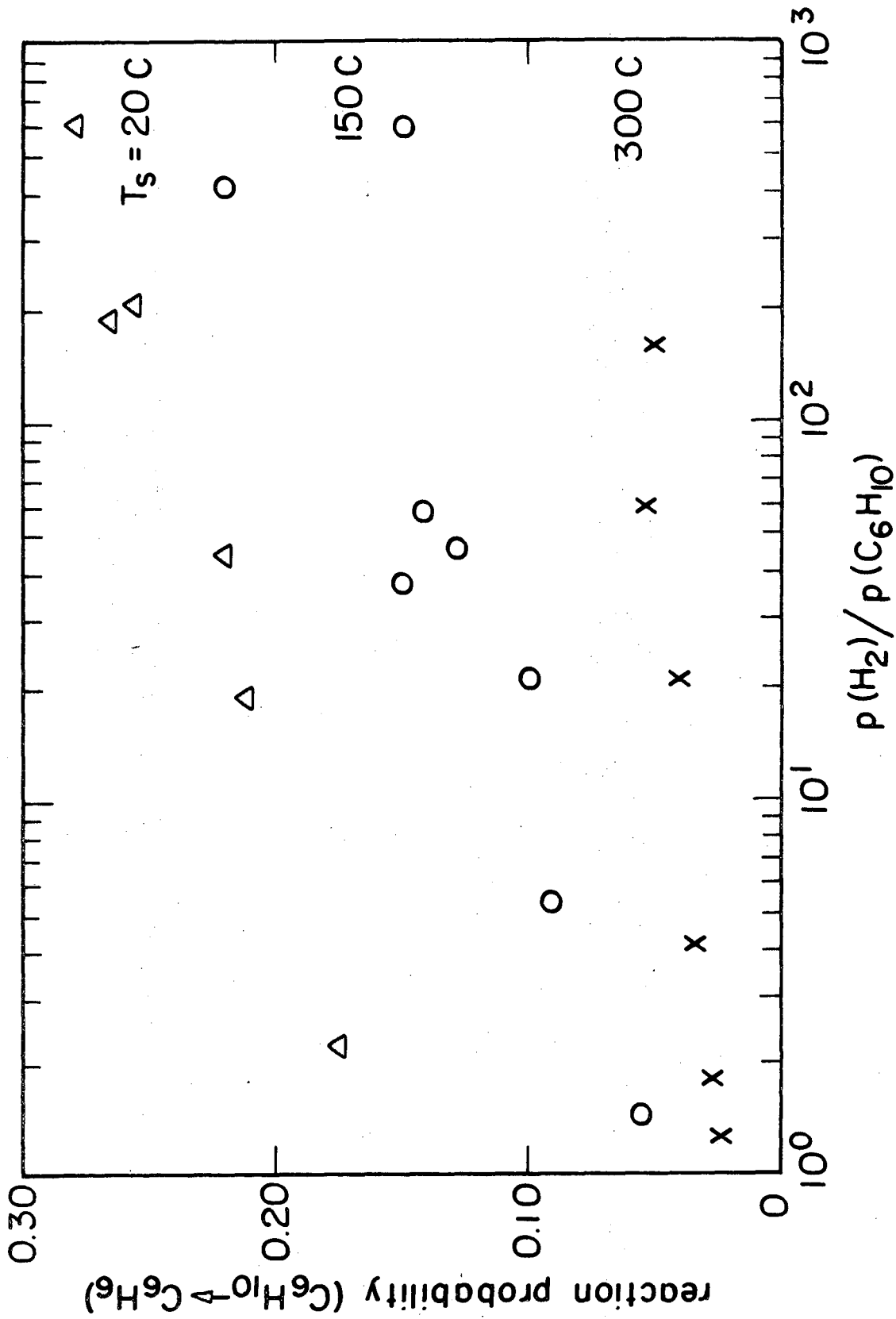
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Figure 1



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Figure 2



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Figure 3

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