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The Adsorption and Surface Reactions of Hydrocarbons on Clean Iridium*

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ABSTRACT

The adsorption of ethane, ethylene and acetylene on clean iridium in a field emission microscope has been found to cause characteristic changes in the work function of the iridium surface. Further changes, which are time and temperature dependent, result when such surfaces are heated. Flash filament experiments have shown that the changes in work function upon heating are due to desorption reactions and that the desorbed product consists principally of hydrogen. By assuming a linear relationship between surface coverage and work function, it has been possible to determine the desorption kinetics from the observed rates of work function change at various temperatures. The results are consistent with a mechanism involving stepwise surface dehydrogenation in which a pair of hydrogen atoms is removed from the hydrocarbon molecule in each step, followed by desorption of the adsorbed hydrogen. At very high temperatures the remaining carbon atoms are removed, presumably by evaporation.

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DISCLAIMER

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The rapid advances in the technology of clean surfaces have given the chemist some hope of eventually understanding the complex gas-surface interactions involved in heterogeneous catalysis. The field emission microscope introduced by Müller[1,2] offers a valuable tool, heretofore largely unexploited, for studying reactions of this type. We have used the field emission microscope to study a very fundamental aspect of catalytic hydrogenation, namely the adsorption and surface reactions of hydrocarbons on transition metal surfaces. Specifically, ethane, ethylene, and acetylene were studied on iridium, a typical catalyst metal.

The image in a field emission microscope results from variations in the intensity of emitted electrons from the various surface regions of the emitter. Adsorption of gas on the surface generally causes changes in both over-all emission and relative emission from neighboring regions on the surface. Thus from changes in the emission pattern one can infer the existence of adsorption and desorption processes. Unfortunately, it is not possible to determine the actual concentration of adsorbed species from these changes. It is, however, possible to follow the rate at which the emission varies and from this obtain information about the kinetics of the surface processes involved. One must proceed cautiously, however, for it is not always clear how changes in emission correspond to changes in coverage.

It should also be noted that information based on changes in emission current is obtained principally from the regions of low work function, generally the high index crystal faces.

The microscope used in this work was so designed that it could be totally immersed in liquid helium.[3] This had the twofold advantage of cooling the emitter and maintaining nearly perfect vacuum conditions. The temperature of the emitter could then be raised to any desired value by electrical heating of the supporting filament, while the resistance of this filament provided an accurate indication of the emitter temperature. The emitter was dosed with the gas to be studied from a molecular beam produced by warming a sidearm containing a small amount of the condensed gas. With this arrangement, gas impinged on the emitter from one side only, and only when the sidearm was warmed. It is important to note that at no time was the adsorbed material in equilibrium with the vapor; desorption was completely irreversible since the gas leaving the surface was taken up by the cold walls of the tube.

The emission patterns resulting from the adsorption of ethane, ethylene, or acetylene and the changes in these patterns resulting from heating have been reported in detail elsewhere.[3] From an analysis of the patterns and work functions resulting from various treatments we have been able to draw a number of conclusions about the interactions of these hydrocarbons with iridium. Ethane is only weakly adsorbed; heating to 100°K is sufficient to desorb most of it, though a small fraction remains which is not removed below 2000°K. Ethylene and acetylene adsorbed above 50°K are strongly bound to the surface, being substantially immobile below 700°K. Ethylene and acetylene adsorbed at 4°K, however, are quite mobile and appear to be only weakly bound. We conclude there is a slight activation energy, ~ 0.1 ev, for strong adsorption of the unsaturated hydrocarbons, which may be associated with opening of the carbon-carbon bond. From about 400° - 700°K both ethylene and acetylene undergo surface reactions which cause marked changes in the work function. Above 700° the decomposition products from both species begin to migrate over the surface and agglomerate, eventually building up sharp ridges before being removed around 2000°K. Below 700° the emission patterns are remarkably uniform, indicating that the surface is fairly homogeneous for adsorption.

Heating iridium covered with ethylene or acetylene caused marked irreversible changes in the work function. Figure 1 shows the changes in work function measured after flashing surfaces covered with ethylene and acetylene to successively higher temperatures for 10 seconds. The curves bear certain similarities, yet there is an additional small peak centered at 250°K observed with ethylene. This peak is quite reproducible, and somewhat more pronounced for very light ethylene coverages.

In order to test whether these work function changes were produced by desorption processes, flash desorption experiments[4,5] were conducted with ethylene on an iridium filament.[6] Evolution of gas from the filament occurred from 250 - 700°K; the pressure rise could partially (but not conclusively) be resolved into two bursts, one from 250 - 400°, the second from 400 - 700°K. The rapid pumping of the desorbed gas by the hot ion gauge filament suggested that the composition of both bursts was principally hydrogen.* Experiments with hydrogen alone showed that it was removed from iridium in the region 250 - 450°K.

On the basis of these results we have proposed[3] that ethylene on iridium undergoes a step-wise dehydrogenation, losing two hydrogen atoms around 300° at a rate controlled by the desorption of hydrogen from the metal. Since the residue from dehydrogenation of adsorbed ethylene at 300°K loses hydrogen above 400°K in the same manner as adsorbed acetylene, it is presumed that this residue is adsorbed acetylene.

In an effort to check this hypothesis we have measured the rate of the work function changes at various temperatures between 400 - 650°K for both ethylene and acetylene. The experiments were conducted by dosing the

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*Note: Preliminary results[7] of experiments using an omegatron mass spectrometer to analyze the desorption products appear to verify our conclusion that hydrogen is the principal desorption product.

microscope tip with hydrocarbon to produce a uniform, saturated layer, then heating the tip to a pre-set temperature until the rate of work function change became very small, interrupting the heating periodically for measurements of emission.

The experimentally determined variations of work function with time and temperature were used to infer the kinetic mechanism of surface reactions by means of the following assumptions and theory:

1. Since work function change $\Delta\varphi$ is our measured quantity rather than fraction of surface θ covered with unreacted species, it is necessary to infer θ from $\Delta\varphi$. We have assumed that θ is related to $\Delta\varphi$; *i.e.*,

$$\theta = \frac{\Delta\varphi_{max} - \Delta\varphi}{\Delta\varphi_{max} - \Delta\varphi_{min}} \qquad (1)$$

   where the extreme values of $\Delta\varphi$ are assumed to correspond to $\theta = 1$ and $\theta = 0$.

2. We assume that the isothermal rate of desorption is given by the Polanyi-Wigner equation

$$-\frac{d\theta}{dt} = \frac{kT}{h}\,\theta^{x}\exp[-\Delta H/RT] \qquad (2)$$

   in which x is the kinetic order of the surface reaction and ΔH is its activation energy.

3. We assume that the activation energy for desorption varies linearly with work function. Higuchi, Ree and Eyring[8] have discussed a theoretical basis for this assumption. In view of assumption 1 this is equivalent to the assumption:

$$\Delta H = \Delta H_o - \alpha\theta \qquad (3)$$

Combining Eqs. 2 and 3 we obtain

$$-\frac{d\theta}{dt} = \frac{kT}{h}\,\theta^x \exp[-\Delta H_o/RT] \exp \alpha\theta/RT \qquad (4)$$

This has the form of the Becker-Zeldovitch equation (9)

$$-\frac{d\theta}{dt} = a\ \theta\ e^{b\theta} \qquad (4a)$$

whose general validity has been discussed by Higuchi, Ree and Eyring.[10] Equation (4) may be integrated to obtain

$$\frac{kT}{h}\exp[-\Delta H_o/RT]t = \begin{cases} F(\gamma_f) - F(\gamma_i) \quad \text{if } x = 1 & (5a) \\ \alpha/RT\left[\dfrac{e^{-\gamma_f}}{\gamma_f} - \dfrac{e^{-\gamma_i}}{\gamma_i} + F(\gamma_f) - F(\gamma_i)\right] \text{if } x = 2 & (5b) \end{cases}$$

where $\gamma_f = \alpha\theta(t)/RT$, $\gamma_i = \alpha\theta(o)/RT$, and $F(x) = \int_x^\infty \frac{e^{-y}}{y}\,dy = -Ei(-x)$

Values of Ei(x), the exponential integral function, have been tabulated.[11]

This treatment was applied to work function-time-temperature data obtained in the temperature range 400 - 700°K, which according to our model should reflect the dehydrogenation of adsorbed acetylene (whether acetylene or ethylene has initially been adsorbed). Equation (1) was used to convert work function data to surface fractions; values of $\Delta\varphi_{max}$ and $\Delta\varphi_{min}$ for ethylene and acetylene were taken from Figs. 1a and 1b, respectively and were substantially the values of $\Delta\varphi$ at 700°K ($\Delta\varphi_{max}$) and 300°K ($\Delta\varphi_{min}$). Dependence of surface fraction of unreacted species on time and temperature thus calculated is presented as experimental points in Figs. 2a and 2b. Values of ΔH_o, α and x were selected to obtain best fits, through Eq. (5), for the experimental data at each temperature. Temperatures and values of the parameters ΔH_o and α are presented in Table 1. The solid curves in Fig. 2 were obtained in this manner. Because the dependence of θ on t at a given temperature reflects a rather small variation in θ, precision in estimation of $\Delta H = H_o - \alpha\theta$ from this dependence is greater than that for estimation of ΔH_o or α only; the data of Table 1 can be used to construct graphs of the variation of ΔH with θ, which according to our model should be linear and the same whether ethylene or acetylene were initially adsorbed. Figure 3 presents such graphs, which are in reasonable agreement with expectation.

The limited variation in θ in kinetic data at a given temperature also made theoretical kinetic isotherms insensitive to the parameter x. In Fig. 2a, for example, curves 1 and 1′ were calculated for first and second order kinetics ($x=1$ and 2) respectively, and (by different choices of ΔH_o and α) can be made substantially coincident. If the same parameters ΔH_o and α are used to calculate curves at a different temperature, the curve calculated using first order kinetics ($x=1$) is in much better agreement with experiment than that calculated using second order kinetics; (compare curves 5 and 5′, calculated using parameters obtained from curves 1 and 1′).

We can suggest three general mechanisms consistent with first order dehydrogenation kinetics. These are

A. $$\underset{**}{\mathrm{HC}}-\underset{**}{\mathrm{CH}} \xrightarrow{k_A} (C_2)_{\mathrm{adsorbed}} + H_2(g)$$

B. $$\underset{**}{\mathrm{HC}}-\underset{**}{\mathrm{CH}} \xrightarrow{k_B} (C_2)_{\mathrm{adsorbed}} + 2\underset{*}{\mathrm{H}}$$

$$2\underset{*}{\mathrm{H}} \xrightarrow{\text{fast}} H_2(g)$$

C. $$\underset{**}{\mathrm{HC}}-\underset{**}{\mathrm{CH}} \xrightarrow{k_C} \underset{**}{\mathrm{HC}}-\underset{**}{\mathrm{C}}\cdot + \underset{*}{\mathrm{H}}$$

a). $$\underset{**}{\mathrm{HC}}-\underset{**}{\mathrm{C}}\cdot \xrightarrow{\text{fast}} (C_2)_{\mathrm{adsorbed}} + \underset{*}{\mathrm{H}}$$

$$2\underset{*}{\mathrm{H}} \xrightarrow{\text{fast}} H_2(g)$$

or b). $$\underset{**}{\mathrm{HC}}-\underset{**}{\mathrm{C}}\cdot + \underset{*}{\mathrm{H}} \xrightarrow{\text{fast}} (C_2)_{\mathrm{adsorbed}} + H_2(g)$$

where the stars denote bonding to the metal.*

These mechanisms lead to identical isothermal rate expressions, and hence cannot be distinguished from isothermal rate data. Various possible transition states can be imagined, however, their plausibilities discussed and corresponding activation energies estimated and compared with experiment. For each mechanism we have calculated activation energies based on the following transition states:

I. Carbon-carbon bonds those of initial state, C-H bond(s) broken, H-H or H-Ir bonds not yet formed

II. Carbon-carbon bonds those of final state, C-H bond(s) broken, H-H or H-Ir bonds not yet formed

III. Carbon-carbon, H-H or H-Ir bonds those of final state in the rate determining process.

While lacking complete knowledge of the bond energies involved, we have made reasonable estimations where necessary. The energies of H-H and C-H bonds were taken as 103 and 98 kcal, respectively (the C-H bond energy was assumed the same as in ethane).[12] The activation energy for desorption of hydrogen from iridium is 17 kcal, while that for adsorption is negligible;[6] from this the hydrogen-iridium bond energy was calculated to be $\frac{1}{2}(17+103) = 60$ kcal. The energy of the carbon-carbon bond

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*We have previously presented arguments for supposing that adsorbed acetylene has an ethane-like structure.[3]

in $(C_2)_{adsorbed}$ was assumed greater than that in $\underset{*}{\mathrm{HC}}-\underset{*}{\mathrm{CH}}$ by an amount equal to the difference between carbon-carbon double and single bond energies, namely 65 kcal.[12] The activation energies calculated from the above data are shown in Table 2.

While such calculations are certainly very approximate, it appears significant that only the energies in column III fall close to the experimental range of 30-46 kcal. Thus to account for this activation energy it is necessary to suppose that the transition state fairly closely approximates the final state in character of bonds formed. If this is so, then mechanism A must be considered unlikely, for it does not seem reasonable that a well developed bond could be formed in the transition state between hydrogen atoms initially on adjacent carbons and therefore initially separated by about 2.5 Å. Furthermore, the desorption of hydrogen from graphite must involve a mechanism similar to A and should therefore require a comparable activation energy. Redmond and Walker[13] recently reported a value of 137 kcal for the removal of hydrogen from graphite at low coverage, which is remarkably close to the calculated energy, 131 kcal, for mechanism A via transition state II.

We conclude that the experimental activation energy can be satisfactorily explained by either mechanism B or C; i.e., the dehydrogenation of ethylene and acetylene involves a surface dissociation followed by desorption of hydrogen.

The activation energy for the dissociation process is approximately equal to the enthalpy; hence the reverse reaction should require a negligible activation energy.

Variation in desorption activation energy with coverage is usually ascribed either to a heterogeneous surface or to changes in bond strength produced by the electric field of the surface double layer.[8] The apparent homogeneity of the iridium surface for hydrocarbon adsorption has been described; hence we attribute the dependence of activation energy with coverage to interaction with the field of the surface dipoles. According to the mechanism we have presented, this interaction must act to decrease the C-H bond energy and/or increase the Ir-H bond energy at high coverage (low work function) in order to decrease the activation energy. Since hydrogen adsorption increases the work function of iridium, the surface field will alter the C-H and Ir-H bond energies in the opposite sense. An increase in work function will then produce an increase in reaction enthalpy and activation energy, as observed.

A rather simple model has been found adequate to explain the changes in field emission from iridium covered with adsorbed hydrocarbons. It would be highly desirable to apply the powerful tools of field ion microscopy and slow electron diffraction to these systems in order to obtain detailed information about surface structure and orientation on an atomic scale. Knowledge of surface structure and surface kinetics is essential for an understanding of catalytic reactions.

ACKNOWLEDGMENT

We are indebted to the Journal of Chemical Physics for permission to republish Figures 1a and 1b.

Table 1. Parameters used in desorption curves of Fig. 2

Curve No.	Temperature	ΔH_o	α
		Ethylene	
1	468 °K	40 kcal	10 kcal
1′	468	39.5	10
2	477	40	10
3	494	40	10
4	502	40	10
5	553	40	10
5′	553	39.5	10
6	579	41.2	12
7	587	41.2	12
8	638	42.5	20
		Acetylene	
A	462	50	20
B	501	48.5	18
C	540	49	18
D	579	47.5	16
E	617	47.4	16
F	656	46.5	14
G	695	46.5	14

Table 2. Activation energies from bond energy data

Mechanism	Activation Energy (kcal) for Transition State		
	I	II	III
A	196	131	28
B	196	131	11
C	98	98	38

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FIGURE CAPTIONS

Fig. 1a - Change in work function with flash temperature for ethylene on iridium.

Fig. 1b - Change in work function with flash temperature for acetylene on iridium.

Fig. 2a - Time dependence of surface coverage at various flash temperatures for ethylene on iridium.

Fig. 2b - Time dependence of surface coverage at various flash temperatures for acetylene on iridium.

Fig. 3 - Variation of activation energy for desorption with coverage.

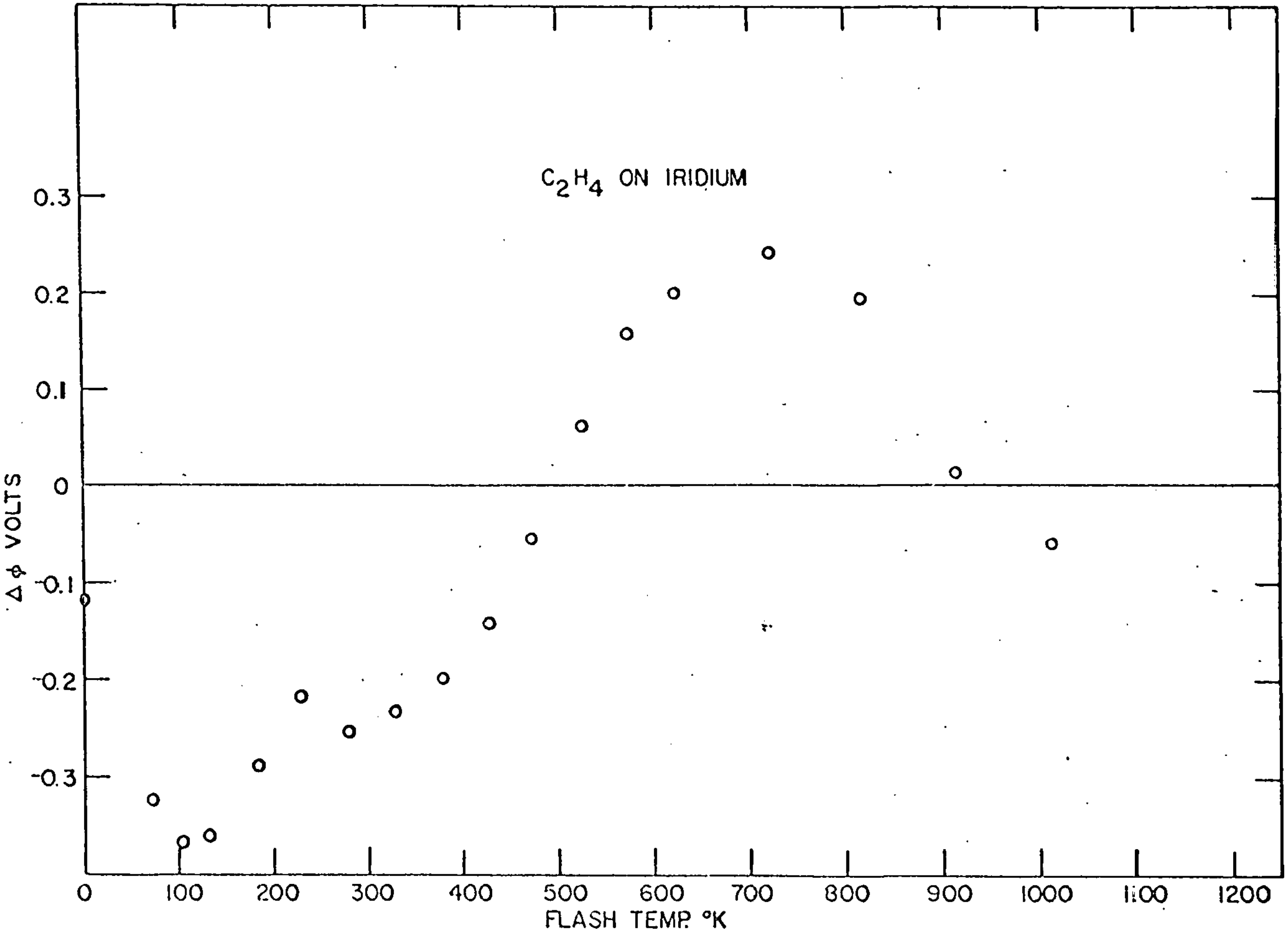

Fig. 1a. Change in work function with flash temperature for ethylene on iridium.

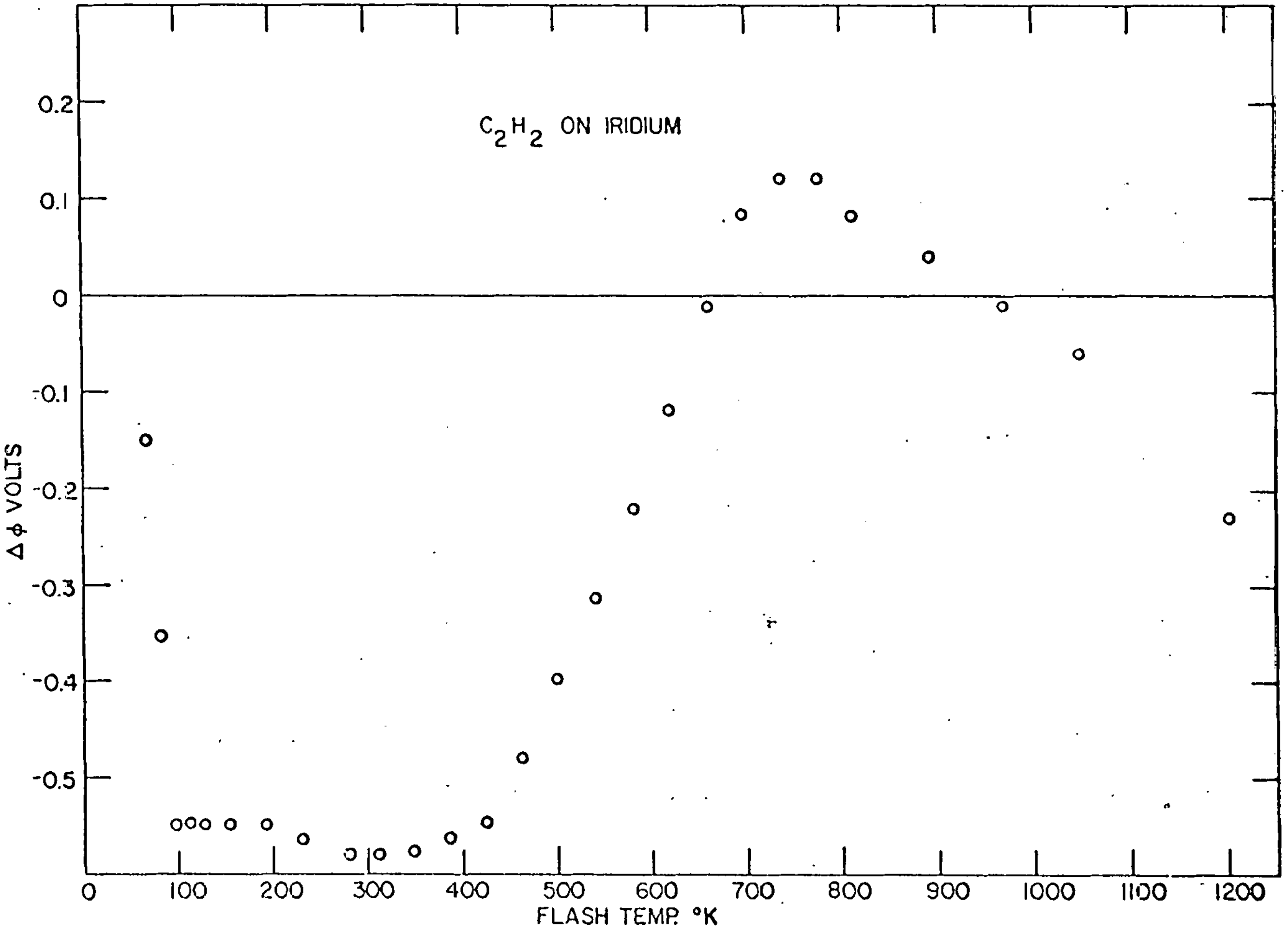

Fig. 1b. Change in work function with flash temperature for acetylene on iridium.

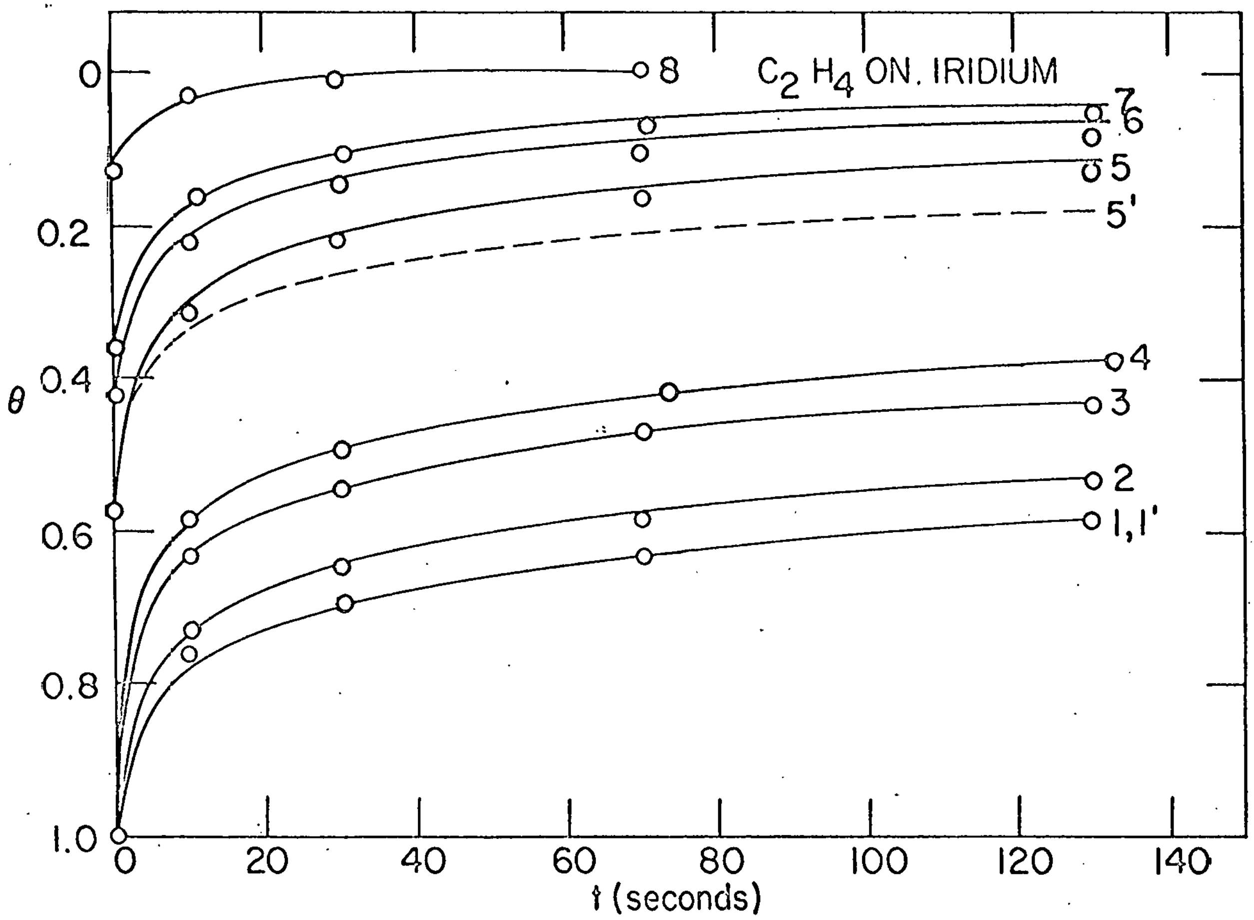

Fig. 2a. Time dependence of surface coverage at various flash temperatures for ethylene on iridium.

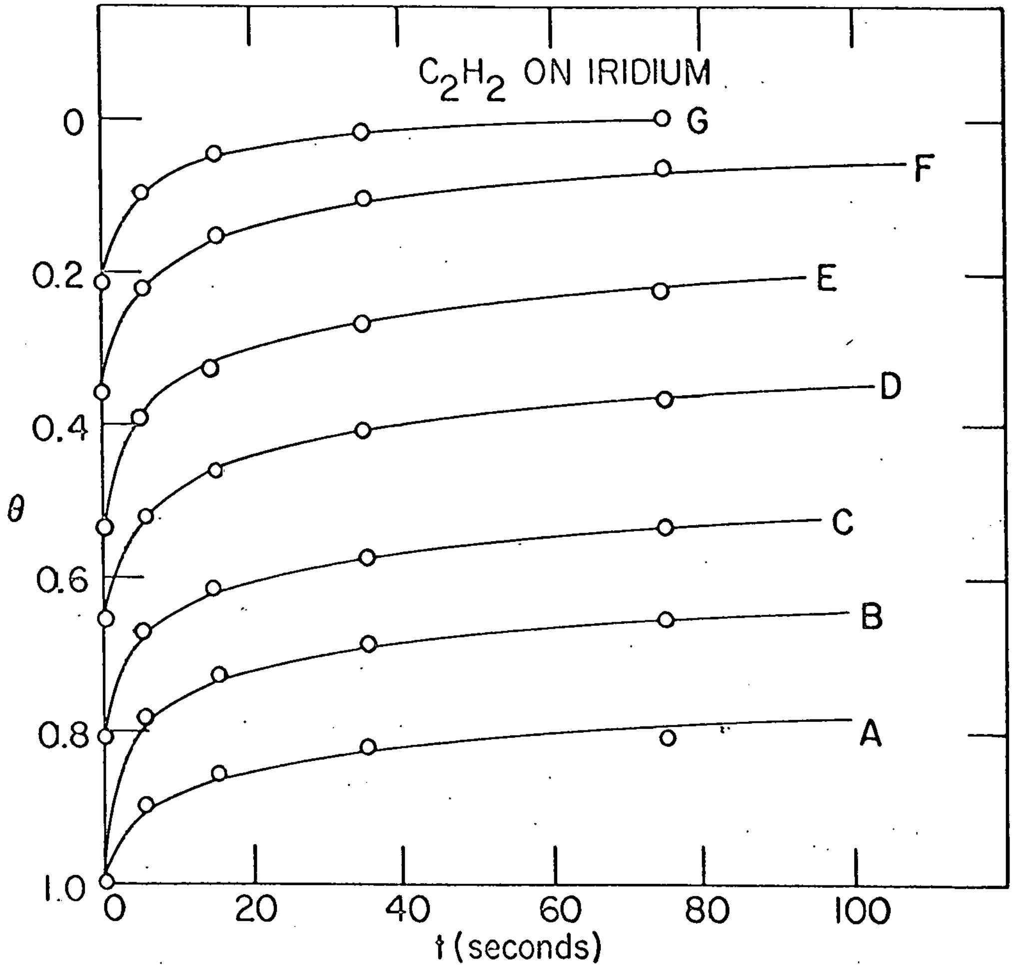

Fig. 2b. Time dependence of surface coverage at various flash temperatures for acetylene on iridium.

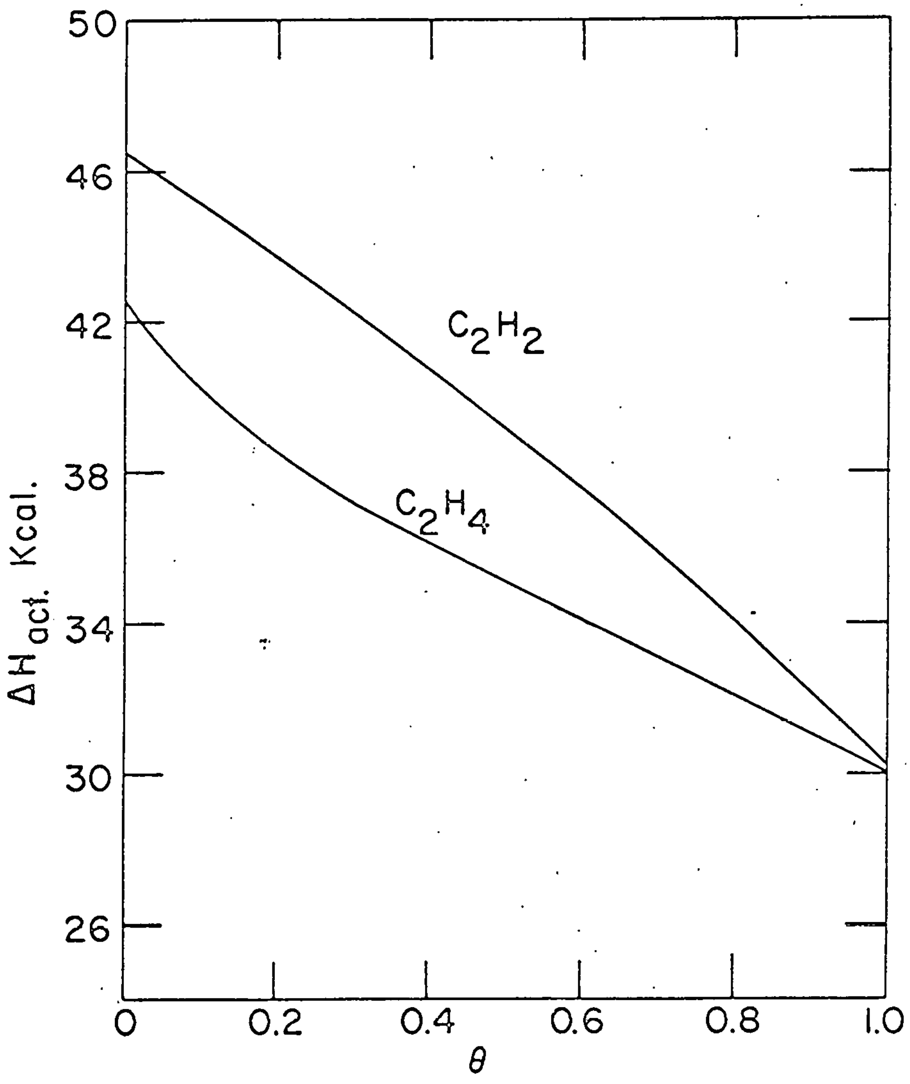

Fig. 3. Variation of activation energy for desorption with coverage.