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ADSORPTION ON PLUTONIUM

PART II: THE LIGHT-WEIGHT HYDROCARBONS

*Larry E. Musgrave
Anthony DiGiallonardo*

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

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ADSORPTION ON PLUTONIUM PART II: THE LIGHT-WEIGHT HYDROCARBONS

Larry E. Musgrave and Anthony DiGiallonardo

Abstract: The sticking probability and surface coverage of methane, ethylene, and ethane molecules impinging on evaporated plutonium films have been measured. The sticking probability shows a rapid decrease from 0.2 to a nearly constant value of 0.01, until full coverage, when a rather rapid decrease occurs. The coverage varies from 14.5×10^{14} molecules per square centimeter for methane, 8.8×10^{14} molecules per square centimeter for ethylene, and 11.0×10^{14} molecules per square centimeter for ethane. Possible bonding mechanisms are discussed.

INTRODUCTION

The sticking probability measurements of gas molecules impinging on clean-metal surfaces in high vacuum, are useful in studying the rate and amounts of gas involved in gas-metal reactions. This report is concerned with the sticking probability and coverage of methane, ethylene, and ethane on evaporated plutonium films.

The first sticking probability measurements were carried out by Becker using a flash filament technique.^{1,2} A filament, usually of tungsten or some other refractory metal, was flash-heated, then cooled and allowed to interact with a gas. Many materials, though, do not form filaments which can be flashed to high enough temperatures for cleaning. Hence, recent work has often utilized evaporated metal films.^{3,4} However, care must be taken when interpreting adsorption data on metal films. Surface roughness, which is common in metal films, may cause the impinging gas to undergo multiple collisions on the surface, or the gas may diffuse into internal pores which will result in erroneously high-measured sticking probabilities.⁵ In addition, care must be taken that the gas molecules are in random motion when striking the metal surface and the ionization gauge so that the true pressure in the volume is measured.^{6,7} At the low pressures used in these studies the mean-free-path of a molecule is large in relation to the volume dimensions. As a result, improper location of chamber openings and gauges may cause gas beaming or shadowing.

This laboratory has undertaken the measurement of the sticking probability and coverage of various gases on evaporated plutonium films.⁸ A large volume in the chamber,

in comparison to the film size, has ensured random motion of the gas molecules impinging on the film and the gauge. The pressure rise in the chamber containing a blank substrate has been compared with the pressure rise in the chamber containing a plutonium film to determine the sticking probability and coverage.

APPARATUS

The apparatus used in this experiment was the same as that used by Adams.⁸ It consisted of a vacuum system, a gas-handling system, an evaporation chamber, and a working chamber. The entire apparatus was made of Type-304 stainless steel. A schematic diagram of the apparatus is shown in Figure 1.

The vacuum system consisted of a mechanical roughing pump and a liquid nitrogen trapped-oil diffusion pump. Pressures in the 10^{-10} torr range were routinely achieved in the system after an overnight bakeout at 400°C.

The gas-handling system contained a gas source and a constant-pressure reservoir. The pressure was held constant in the reservoir by means of a servo-operated ultra-high vacuum valve controlled by an automatic-pressure controller. The gases used were reagent grade and were contained in glass bottles. The constant-pressure reservoir was separated from the working chamber by an ultra-high vacuum valve.

The evaporation chamber contained a tantalum boat which was resistively heated by a high-current power supply. It was designed so that a reproducible geometric area of plutonium could be evaporated onto a glass slide in the working chamber. The evaporation and working chambers were separated by an electromagnetically operated stainless-steel slide valve.

The evaporation chamber could be connected directly to the diffusion pump to outgas the plutonium while preventing contamination from entering into the working chamber. The working chamber had a volume of 1.2 liters and contained a glass slide onto which a circular plutonium film with an area of 0.816 cm² was

Figure 1. Schematic of Sticking Probability Apparatus.

evaporated. A glass window allowed visual observation on the glass slide. A Bayart-Alpert type ionization gauge connected to a millivolt self-balancing recorder continuously monitored the pressure in the working chamber.

OPERATION

Following bakeout, the plutonium and ionization gauges were outgassed. After the plutonium and gauges had cooled, the constant-pressure reservoir was filled and opened to the working chamber. This allowed the walls of the working chamber to become saturated so that they would not pump during the experiment. The working chamber was evacuated and then opened to the constant-pressure reservoir. The resulting pressure-versus-time curve was recorded. The working chamber was again evacuated and opened to the evaporation chamber where plutonium was evaporated onto the glass slide. The working chamber was again opened to the constant-pressure reservoir and the resultant pressure-versus-time curve recorded.

CALCULATIONS

The pressure-versus-time curves obtained with a bare substrate and an adsorbing plutonium surface were compared. The sticking probability as a function of coverage, and the coverage-versus-exposure, were determined using the following relations.

The rate of flow of an ideal gas into a chamber can be found by differentiating the ideal gas law.

$$\frac{dN}{dt} = \frac{N_0 V}{RT} \frac{dP}{dt}, \quad (1)$$

where dN/dt is the rate of molecules entering the chamber,

N_0 is Avogadro's number,

V is the working chamber volume,

R is Rydberg's constant,

T is absolute temperature.

When it is assumed that the walls and the gauge are not pumping, the rate of gas being adsorbed on the metal film is

$$\frac{dN_a}{dt} = \frac{dN_{in}}{dt} - \frac{dN_v}{dt}, \quad (2)$$

where

$\frac{dN_a}{dt}$ is the rate of molecules entering the chamber, which are adsorbed

$\frac{dN_{in}}{dt}$ is the rate of all molecules entering the chamber, and

$\frac{dN_v}{dt}$ is the rate of molecules entering the chamber, which are not adsorbed.

Hence,

$$\frac{dN_a}{dt} = \frac{N_0 V}{RT} \left(\frac{dP_{in}}{dt} - \frac{dP_v}{dt} \right)^* \quad (3)$$

and

$$S = \frac{\frac{dP_{in}}{dt} - \frac{dP_v}{dt}}{\frac{dP_v}{dt}}, \quad (4)$$

where S is the sticking probability.

A computer program has been written which carries out the necessary computations.⁹ The necessary input data is the pressure at a constant-time interval. The output includes sticking probability, total number of molecules adsorbed, and exposure.

RESULTS AND DISCUSSION

Tables I through III give the total number of gas molecules adsorbed per unit of geometric surface area, the initial sticking probability, the pressure in the constant-pressure reservoir, and the pressure measured in the working chamber during evaporation of the plutonium for each experimental run. The average value and

standard deviation of the total number of molecules adsorbed per unit of geometric surface area, and the initial sticking probability for each gas are also listed. Certain runs in which a sticking probability much greater than one, or in which an evaporation pressure greater than 5×10^{-6} mmHg was noted, are not included in the tables.

The impossible values of sticking probability which are especially noted during measurements at vacuums in the high 10^{-5} torr range were the result of manually opening the valve between the constant-pressure reservoir and the working chamber. The initial-pressure rise was not reproducible when the valve was manually opened and, hence, the initial sticking probability was incorrect.

This problem, although not so severe, extended to the lower pressures.

The high pressure values recorded during plutonium evaporation usually occurred with plutonium which had not been previously evaporated. Hence, the pressure rise probably was due to released contaminants. This interpretation is supported by a lessening in film activity.

Table I. Values of initial sticking probability, total number of molecules adsorbed per unit geometric surface area, pressure of the constant-pressure chamber, and pressure during evaporation for methane on plutonium. Numbers not listed were deviant runs.

Run	Initial Sticking Probability	Total Adsorbed per $\text{cm}^2 \times 10^{-14}$	Constant Pressure $\times 10^6$	Evaporation Pressure $\times 10^6$
1	0.587	10.55	9.5	3.0
2	0.905	16.34	9.5	1.5
4	0.853	15.75	9.5	1.5
5	0.081	18.80	9.2	3.0
6	0.144	17.21	9.2	3.5
7	0.203	15.63	9.2	2.5
8	0.156	12.20	9.2	2.0
9	0.194	12.04	9.2	2.0
10	0.473	16.24	9.2	2.6
11	0.331	13.30	9.2	2.6
12	0.905	16.70	9.2	2.0
15	0.122	16.01	6.0	2.3
19	0.169	11.23	7.5	5.3
20	0.099	14.35	7.5	3.0
22	0.069	13.20	7.5	2.4
23	0.156	12.80	7.5	1.9
25	0.151	14.27	7.5	3.3
26	0.232	13.86	7.5	2.0
	0.247	15.38	9.0	3.4
Average	0.320	14.47		
Deviation	0.284	2.16		

*Equation (3) can be integrated to give the total number of molecules adsorbed.

Table II. Values of initial sticking probability, total number of molecules adsorbed per unit geometric area, pressure of the constant-pressure chamber, and pressure during evaporation for ethylene on plutonium.
Numbers not listed were deviant runs.

Run	Initial Sticking Probability	Number Adsorbed per $\text{cm}^2 \times 10^{-14}$	Constant Pressure $\times 10^6$	Evaporation Pressure $\times 10^6$
1	0.140	9.19	9.0	0.1
6	0.410	10.64	9.0	2.5
4	0.548	12.47	9.0	2.5
6	0.768	10.93	9.0	1.9
7	0.446	11.18	9.0	4.7
8	0.572	8.99	9.0	2.0
9	0.403	7.05	9.0	2.2
10	0.404	6.69	9.0	1.5
11	0.384	8.05	9.0	2.3
12	0.378	8.72	9.0	1.8
13	0.329	9.68	9.0	2.4
14	0.235	7.93	9.0	1.8
15	0.126	9.42	10.0	3.8
16	0.292	7.93	12.0	2.3
17	0.194	9.31	10.0	3.6
20	0.100	8.37	4.0	2.2
31	0.272	8.71	4.0	3.2
22	0.093	8.03	4.0	2.2
23	0.135	8.15	4.0	2.1
24	0.082	7.73	4.0	2.0
25	0.078	8.33	4.0	1.8
27	0.302	9.21	2.0	1.2
23	0.323	10.35	2.0	1.0
30	0.095	4.86	1.5	0.9
31	0.011	6.99	1.5	0.6
Average	0.289	8.76		
Deviation	± 0.186	± 1.61		

Contamination to a lesser extent may have affected some of the listed runs.

The deviation of the values of sticking probability and total number of molecules adsorbed per unit area is related primarily to the problems of manual valve opening and released contaminants. In addition, some of the deviation in the total numbers of molecules adsorbed may be due to variations in the thickness of the evaporated film. Evaporated films may contain some internal pores into which adsorbed gases diffuse. The number of pores would vary with thickness as well as geometric area. The film thickness was not measured in this experiment; therefore, the variation of total molecules adsorbed with thickness could not be determined.

For ethane and ethylene the initial sticking probability and the amount adsorbed tends to be slightly lower at lower pressures. The slight lowering is probably caused

Table III. Values of initial sticking probability, total number of molecules adsorbed per unit geometric area, pressure of the constant-pressure chamber, and pressure during evaporation for ethane on plutonium.
Numbers not listed were deviant runs.

Run	Initial Sticking Probability	Number Adsorbed per $\text{cm}^2 \times 10^{-14}$	Constant Pressure $\times 10^6$	Evaporation Pressure $\times 10^6$
1	0.061	8.36	9.0	1.2
2	0.429	14.68	9.0	0.6
3	0.216	10.34	9.0	0.8
4	0.393	10.32	9.0	0.7
5	0.318	9.91	9.0	7.0
6	0.306	12.49	9.0	1.5
7	0.274	14.63	9.0	1.2
8	0.131	11.63	6.0	1.0
9	0.235	11.66	6.0	0.6
10	0.099	10.76	6.0	5.0
11	0.219	14.41	6.0	3.0
12	0.072	8.85	6.0	2.5
13	0.145	11.12	4.0	1.2
14	0.167	10.78	4.0	2.5
15	0.189	11.06	4.0	3.0
16	0.110	9.66	4.0	2.5
17	0.179	8.47	1.6	3.0
19	0.159	8.81	1.6	2.5
20	0.164	9.89	1.6	2.0
21	0.373	9.68	1.6	3.0
22	0.408	12.49	15.0	1.9
23	0.218	11.14	15.0	1.4
24	0.515	13.05	15.0	1.2
25	0.285	11.44	15.0	1.2
Average	0.232	11.07		
Deviation	0.117	± 1.84		

by an experimental artifact and is not an actual lowering. It is related to the previously discussed problem of manually opening the valve between the constant-pressure chamber and the working chamber.

Figures 2 through 4 show the variation of sticking probability with coverage for methane, ethylene, and ethane on plutonium. The values shown are averages for the various runs.

Figures 5 through 7 show the number of molecules adsorbed versus exposure. The curve is an average of the various runs.

The general shapes of the sticking probability-versus-coverage curves are similar for methane, ethylene, and ethane, and also for hydrogen.⁸ The sticking probability initially falls rapidly, then levels off until nearly complete coverage.

Figure 2. Sticking Probability of Methane.

Figure 3. Sticking Probability of Ethylene.

Figure 4. Sticking Probability of Ethane.

Figure 5. Total Molecules Adsorbed per Unit Area versus Exposure of Methane.

Figure 6. Total Molecules Adsorbed per unit Area versus Exposure of Ethane.

Figure 7. Total Molecules Adsorbed per Unit Area versus Exposure of Ethylene.

The number of molecules adsorbed appears to approach a limit with continued exposure. This limit should correspond to a monolayer coverage. The number of gas molecules can be compared with the number of plutonium atoms on an ideal surface in an attempt to understand the possible chemisorption bonding.

If the average spacing between plutonium atoms in the bulk is assumed to be the spacing at the surface, then there are about 12.8×10^{14} plutonium atoms on one square centimeter surface. Of course, evaporated films have varying degrees of roughness. Hence, there are probably more plutonium atoms on the film surface than given by the assumption.

About 14.5×10^{14} methane molecules, 8.7×10^{14} ethylene molecules, and 11.1×10^{14} ethane molecules were adsorbed on one square centimeter of plutonium surface. The number of methane molecules adsorbed is greater than the number of plutonium atoms on an ideal surface. It is unlikely that more than one molecule of methane is associated with one atom of plutonium, so it is likely that the surface is rough, as mentioned. Assuming a 1 to 1 ratio of molecules-to-atoms the roughness factor would be about 1.1. However, in studying the bonding mechanism of methane with other metals, researchers have found that chemisorption often dissociates methane, and hydrogen is found in the gas phase.¹⁰ Hydrogen is chemisorbed by plutonium⁸ so it is possible that hydrogen also is attached to surface plutonium and occupies some surface sites. If the hydrogen is chemisorbed, then the surface is rougher than stated previously.

The surface bonding of ethane and ethylene has been shown to vary with the substrate.¹⁰ Assuming that there are slightly more than 14.5×10^{14} plutonium atoms on one square centimeter of surface, it appears that ethylene is adsorbed onto two surface-plutonium atoms. Two-site adsorption has been observed with other metals¹¹ but there is discrepancy over whether C=C or C-H bonds break. If C-H bonds break, hydrogen may be released. Released hydrogen has been observed to form ethane in the gas phase over nickel.¹² Studying the residual gas over plutonium may clarify the bonding of ethylene.

The number of ethane molecules adsorbed on a plutonium surface is greater than the number of ethylene molecules adsorbed. This suggests that a different adsorption mechanism is involved. Previous work has shown that ethane adsorption seldom involves breaking of C-C bonds,

but it does involve the breaking of one or two C-H bonds and the attachment of the radical to one or two surface-metal atoms, depending upon the site energy.¹³ This would explain the observed number of molecules adsorbed. Study of the gas phase could give further information of the adsorbed specie.

These assumptions, that (1) an evaporated plutonium surface is rough containing more than 14.5×10^{14} atoms per square centimeter, (2) a methane radical adsorbs onto a single surface plutonium atom with breaking of C-H bonds, (3) an ethylene radical adsorbs onto two surface plutonium atoms with probable breaking of C=C bonds, and (4) ethane radicals adsorb to one or two plutonium surface atoms with breaking of C-H bonds – are highly tentative and further study is needed. Study of the residual gases will give a lower limit of released hydrogen and also will show if ethane is being formed during ethylene adsorption. Infrared spectra will be useful in determining the structure of adsorbed complexes.

CONCLUSION

Sticking probability and coverage measurements of methane, ethylene, and ethane on thick plutonium films show that these light-weight hydrocarbons actively adsorb onto plutonium.

The sticking probability initially falls rapidly to a nearly constant value of 0.01 until saturation for all three gases. At saturation the sticking probability falls to values too low to measure. The coverage at this point is assumed to correspond to a monolayer of adsorbed gas.

Slightly more molecules of methane are adsorbed than the number of plutonium atoms in an ideal surface. This suggests bonding of methane radicals to single plutonium surface atoms and possible release of hydrogen. About one-half as many molecules of ethylene are adsorbed as methane on a plutonium surface. The number suggests two-site attachment of the ethylene radical with little release of hydrogen. The number of ethane molecules adsorbed is intermediate between the number of methane and ethylene molecules adsorbed on plutonium. Thus, a combination of one- and two-site attachments of the ethane molecule is suggested. This type of attachment would likely release some hydrogen. Further study of the residual gases and the infrared spectra are needed to clarify the bonding.

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