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A Molecular Beam Study of the Effect of Temperature on a Surface Reaction: Displacements by an Acetylene Beam of Species from ^{14}C-Ethylene-Covered Palladium

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This paper describes the development of a molecular beam apparatus for the study of interactions of gases at solid surfaces in systems of catalytic interest. The apparatus has been used in an investigation of the displacement, from palladium films, of the surface species resulting from the adsorption of ^{14}C-ethylene by a beam of acetylene. The fate of the isotopically labeled species was followed in desorption into vacuum and in beam displacement. The detector for radioactivity was a solid state detector mounted close to the target inside the beam system. The beam source temperature could be varied between 15 and 350°C, and the target between 15 and 90°C. One of the principal aims of the study was to find the effect on the displacement reaction of changing the surface and beam temperatures independently. Increased rate of displacement resulted when target temperature was increased, but not when beam temperature was increased.

In both vacuum desorption and displacement experiments three stages were observed. A fast desorption or displacement stage was followed by a slower step, while a third phase was retained on the surface.

INTRODUCTION

Molecular beams have been used in the study of a variety of surface processes (*1*) but until now they have not been applied to the study of heterogeneous catalysis. The potential of the beam method in this field lies in the dynamic character of the experiments, which thus bear a close resemblance to catalysis, and in the possibility of isolating parameters in fundamental surface studies.

When the beam method is combined with surface-radioactivity measurements there is the added advantage of being able to follow a sequence of events occurring on a surface such as adsorption, desorption, or replacement of molecules. In our exploitation of this approach we have investigated the effect of temperature on a surface process. This is normally expressed in catalysis in the familiar form, $k \approx A \exp(-E/RT)$. What is possible in the beam system is to be more precise about the influence of the temperature: we can find out whether it is the temperature of the gas molecules involved in the reaction, or the temperature of the surface, which affects the rate of reaction. We examined this problem in our molecular beam apparatus by selecting independent temperatures for the beam, and for the surface.

The choice of a reaction presented problems, for the flux of molecules in a typical beam on 1 cm^2 of a target is about 10^{13} to 10^{14}/sec, equivalent to a reactant pressure of $\sim 10^{-7}$ Torr: normal studies in catalysis are performed at pressures of 0.1 to 100 Torr. Thus we had to find a reaction which would proceed at measurable rates at very low pressure. We chose a displacement reaction in which a surface was first exposed to ethylene-^{14}C: the labeled species on the surface was then displaced by a beam of

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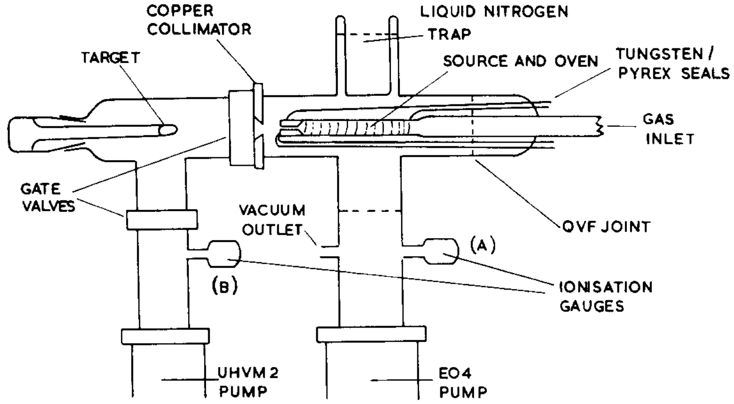


FIG. 1. Outline drawing of molecular beam apparatus.

molecules of acetylene. The surface was freshly evaporated palladium, and chemisorption and displacement were to be observed directly by a solid state detector sensitive to ^{14}C-β particles.

It was first necessary to examine the desorption behavior of ethylene-^{14}C covered surfaces into vacuum. After this, we could study the effect of molecular beams of acetylene from a source at temperature T_1 impinging on targets at temperature T_2.

EXPERIMENTAL METHODS

The main problem in designing the system arose from trying to reconcile the high beam intensity, required for reasonable reaction times, with the need for a good vacuum in the system. The vacuum had to be such that scattering of the beam was negligible and spurious molecular collisions with the target were minimized. Thus differential pumping, and an orifice for production of the beam which gave partial collimation, were incorporated in the design.

DESCRIPTION

The apparatus Fig. 1 was constructed of 3-in. diam. QVF glass units, glass/Kovar graded seals being used for connections to stainless steel flanges for pump connections. (A) and (B) represent Edwards IG3G Bayard-Alpert gauges.

The beam source Fig. 2 consisted of a copper tube, 1 cm internal diameter, with an orifice 26 mm long 2-mm internal diameter. The tube was internally baffled to ensure thermal equilibrium of the beam gas. The source chamber could be heated electrically through Nichrome tape, and its temperature measured by means of a copper/constantan thermocouple.

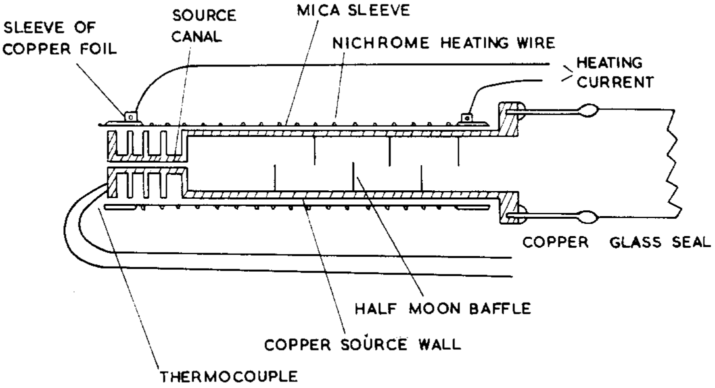


FIG. 2. Beam source.

The source exit was 3.4 cm from the 6-mm diameter hole in a ¼-in. copper plate which served as a collimator. The beam entered the target chamber through a VAT N.W.65 gate valve, Fig. 3.

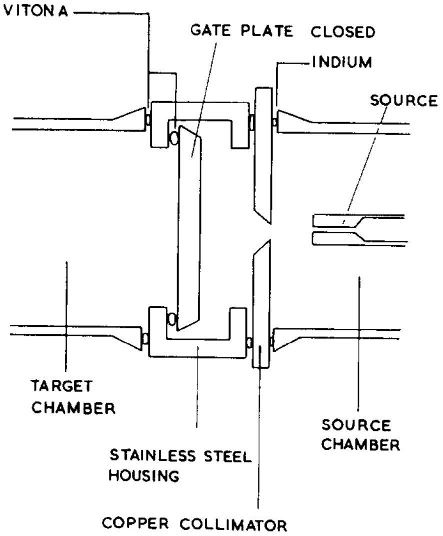


FIG. 3. Source, collimator, and gate valve.

Gas inlet to the beam source was from reservoirs via a variable leak needle valve. Gas pressure in the source was measured by a calibrated Edwards G5C2 Pirani gauge.

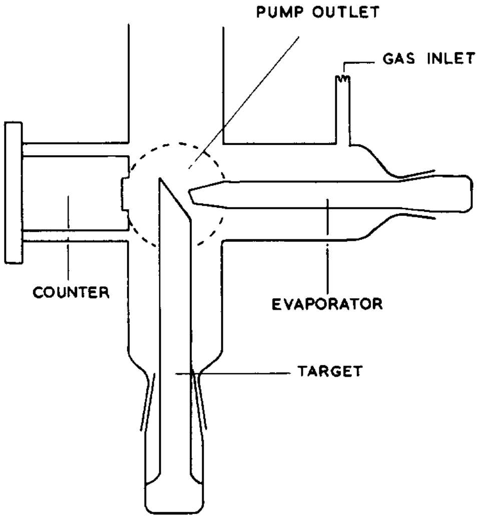


FIG. 4. Target chamber.

The target chamber, Fig. 4, was connected to a UHVM2 mercury diffusion pump via a VAT N.W.65 gate valve, a liquid-nitrogen trap, and a Peltier-cooled baffle. Pressure was measured by an Edwards IG3G Bayard-Alpert gauge.

The source chamber was connected to an unbaffled, untrapped, Edwards EO4 4-in. oil diffusion pump which used Silicone 705 as the pump fluid. In this chamber contamination was secondary in importance to achieving maximum pump speed. A liquid-nitrogen trap was placed opposite the pump orifice to cut down contamination by oil backstreaming. In this way, and by mild baking prior to operation of the molecular beam, a background pressure of 5×10^{-9} Torr was regularly achieved in the source chamber which should not have contributed at all significantly to contamination of the surface under investigation in the target chamber.

The evaporator can throw a palladium film onto a 1-cm diameter area of the glass target, Fig. 5. The target can then be turned to face the detector. The target was hollow, and through it circulated water from a thermostated tank. Up to 70°C the temperature recorded on the thermocouple inside the target was the same as that of the water bath. Film weights produced were 0.1 to 0.2 mg.

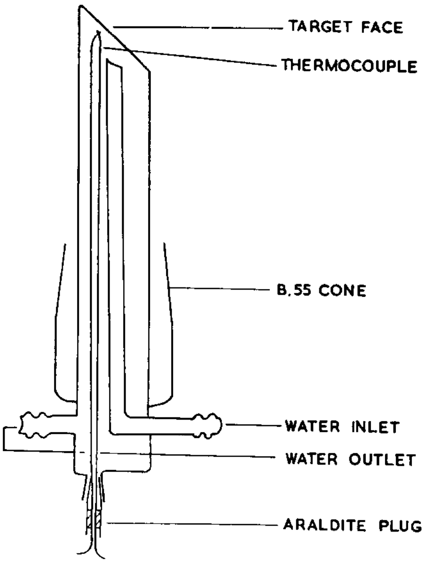


FIG. 5. The target assembly.

The filament for evaporation was

mounted by means of stainless steel connectors to the tungsten rods which carried the heating current. When the target was turned to face the counter it screened the counter from any radioactivity subsequently adsorbed inside the evaporator.

Radioactivity Measurements

The requirements for the detector for radioactivity were that it should be compatible with incorporation into a UHV system and that it should be effectively windowless from the point of view of high sensitivity for β-detection (^{14}C, E, β max 156 keV). If we set a lower limit of 3 counts/sec in the final scaler and assume that geometry discrimination and absorption losses make the system only 1% efficient, then only 10^{14} molecules on the surface are required for detection. This should be compared with the likely number of $>10^{15}$.

The solid state detector was a Simtec L. C. 50-0.5-27 with an active area of 50 mm^2 and a depletion depth of 0.5 mm. An Elliot Electronics Tubes Ltd. S.R.D. 15 of area 1.5 cm^2 and depletion depth 500 μ was also used. They were mounted on telescopic copper tubes which permitted them to be set close to the target. The copper tubes also provided a coaxial shield against interference pickup.

The associated electronics for bias, amplification and pulse analysis consisted of Nuclear Enterprise units NE 5383, 5321, 5283, 5259, 5199. Pulses from the analyzer could be fed to a rate meter and pen-recorder, a scaler, or a Laben 400-channel analyzer. An anticoincidence system had to be incorporated in the system to eliminate random impulsive interference. The normal background of the complete system was 20 to 30 cpm for the Simtec detector, 120 for the Elliot detector: these could rise to 400 cpm from static interference.

This interference was entirely eliminated by picking it up on an aerial, amplifying it, and using the signals to cancel the spurious pulses generated in the solid state detector system (*2*). With this anticoincidence unit the background, over 60 hr, was never above 30 cpm. The solid state detection system had excellent vacuum properties but was light sensitive: the apparatus had to be operated in total darkness. The detector had no window problems, had a high detection efficiency for ^{14}C-β particles and good background characteristics. The noise stability of the solid state devices used deteriorated over a period of months, probably because of operating them at what, for them, was a fairly high temperature. Constant resetting of bias levels did however make the noise levels tolerable.

Materials

Three-in. diameter Quickfit Visible Flow (QVF) Pyrex glass units with 3-mm walls, flanged ground glass ends, were bolted together to give a robust assembly, easy to dismantle and modify. The gaskets between units were of $\frac{1}{16}$-in. diam indium wire (Johnson Matthey and Co. Ltd.). All units were annealed at 530°C before construction of the system. The assembled system could be baked repeatedly to 150°C during evacuation.

Where materials not commonly used in UHV work were present, Apiezon N grease and Araldite, these were outgassed *in situ* over long periods.

Ethylene and acetylene were purified by condensation and pumping. Samples were examined by mass-spectrometry and GLC and found to have a purity better than 99.5%. Ethylene-^{14}C, from the Radiochemical Centre Amersham, was 99% pure as ascertained by GLC.

Calculation of Performance

The highest source pressure which could be used was dictated by the requirement that the mean free path of the gas in the source must be equal to or greater than the length of the exit canal. For acetylene at 300°K this pressure was 2×10^{-3} Torr.

The expected total outflow of acetylene from the source at this pressure was 2.5×10^{15} molecules sec^{-1}. The effective pump speed of 180 liters sec^{-1} in the collimator chamber gave a residual pressure of 4×10^{-7} Torr. The inflow into the target chamber arose from two sources: diffusion from the source chamber and from the beam gave 4.4×10^{13} and 1.92×10^{14} molecules sec^{-1}, respectively. The effective pump speed in the target chamber of 60 liters sec^{-1} produced a residual pressure of 1.1×10^{-7} Torr. Thus 4.4×10^{13} molecules from residual gases struck unit area in the target chamber per second. 1.92×10^{14} molecules from the beam struck the target, and covered an area of diameter 2.7 cm. The evaporated metal spot had a diameter of 1 cm, and this ensured that the collimation was effective. 3.7×10^{13} molecules struck unit area of the metal spot per second. The beam:background strike ratio at the surface was 1:1.1.

When air was used as a source gas to test the calculations and the behavior of the systems, it was introduced into the source at 2×10^{-3} Torr. The pressures recorded in the source and target chambers were 2.47×10^{-7} and 7.0×10^{-8} Torr, respectively.

These values are about one half of those predicted, viz, 4.0×10^{-7} and 1.1×10^{-7} Torr. The ionization gauges were located approximately halfway between the pumps and the chambers; there the pump speed was higher, by a factor of about two: the recorded pressures would thus be halved. Good agreement was thus obtained between the calculated and experimentally determined performances of the system.

Procedure

We shall describe a typical experiment in which the performance of the apparatus was compared with the predicted behavior. The experiment involved the precovering a palladium film with ethylene-^{14}C and observing the effect of an acetylene beam on the surface. The surface was at 25°C, the beam source was 60°C.

Target and source chambers were baked at 140°C and evacuated. Ionization gauges were degassed at 250°C and the beam source at 200°C. The target chamber, which was isolated from the source chamber, was cooled and pumped out for 24 hrs: the pressure was 5×10^{-9} Torr.

During this period the source chamber was still being baked and pumped. The palladium wire, Johnson Matthey and Co. Ltd. grade-pure, 0.02 in diameter, was degassed by passing a current of 5.5 A through it for 30 min, with occasional 10-sec periods at 7.0 A. Further degassing took place overnight at 4 A. The final pressure in the target chamber was 5×10^{-9} Torr. The source chamber was then cooled, its liquid N_2 trap filled and the source oven temperature adjusted to 60°C.

The counter background was determined. The needle valve on the gas reservoir system was opened to give a pressure of acetylene in the source of 2.1×10^{-3} Torr as measured on a Pirani gauge calibrated against a McLeod gauge for air, acetylene, and ethylene. The ionization gauge recorded a pressure of 2×10^{-8} Torr. The gate valve to the target chamber remained closed.

The gas to be introduced into the target chamber was then prepared so that the ethylene pressure for precovering of the palladium (*3*, *4*) would be between 8 and 10×10^{-2} Torr. The palladium film was then thrown onto the target at 15°C, by passing 6.8 to 7.0 A through the filament for 5–15 min. Pressure rose to 3×10^{-7} Torr. The gate valve to the pump was closed and ethylene-^{14}C was admitted to the target and the equilibrium pressure was recorded. After 4 min the surplus ethylene was removed by condensation, the room was darkened, the ionization gauge switched off and the counter switched on to follow the removal of ethylene-^{14}C. At this stage the counter saw only the gas phase. The count rate dropped to 2000 cpm and at this point when the ethylene pressure was 4×10^{-4} Torr, the gate valve to the pump was opened to pump away residual ethylene. The pressure at this stage was 1×10^{-8} Torr. The count rate dropped to background.

The target was turned to present the ^{14}C covered surface to the counter. The count rate was then observed for 30 min and the target temperature then was raised to 25°C.

The gate valve to the source chamber

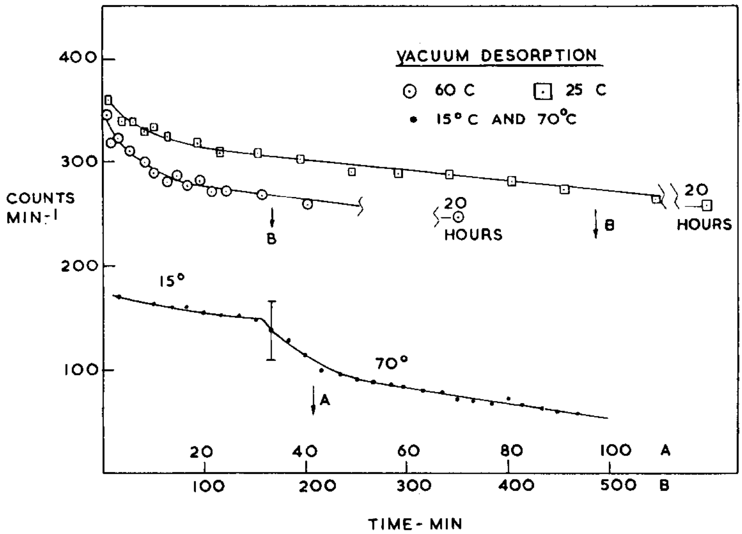


Fig. 6. Desorption into vacuum of species from palladium films covered by ^{14}C-ethylene: count rate from surface versus time.

was then opened and the beam fell on the surface. The count rate from the surface was recorded by means of a scaler and ratemeter or on a Laben-multichannel analyzer, used in the multiscaler mode with print-out.

Checks were made throughout the run on source temperature and pressure.

Results

In the first three experiments, Fig. 6, ethylene-^{14}C was adsorbed on palladium at 15°C and the desorption of the surface species into vacuum was observed. The surface temperatures were 25 and 60°C and in the third experiment the surface

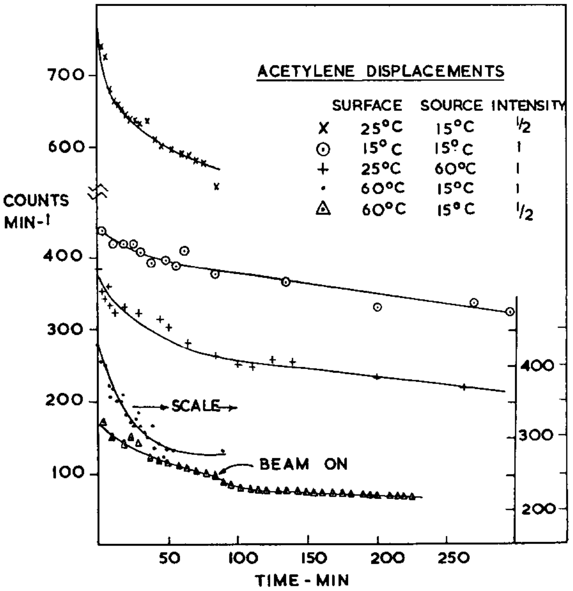


Fig. 7. Displacement by a beam of acetylene molecules of ^{14}C-species on palladium; palladium surfaces precovered by ^{14}C-ethylene.

temperature was 15°C for the first 33 min, then 70°C for the remainder of the time.

Figure 7 shows the displacement of species by acetylene beams striking the target. Variations were made with the surface temperatures at 15, 25, and 60°C and the beam source at 15 and 60°C. In two of the experiments the beam was run at half intensity, Fig. 10.

DISCUSSION

The primary purpose of an examination of the results was to establish the rates at which desorption occurred in vacuum and to compare these with rates of displacement by acetylene beams. The second aim of the analysis of the results was to find out whether temperature of target or temperature of the beam source had the largest effect upon rates of displacement.

In order to compare the results, we sought a method of displaying them which would give linear plots from which comparative slopes could be obtained. We also set the criterion that there should be the minimum number of steps in handling the data to avoid errors and subjective choices.

Linear plots resulted when we plotted N against $t^{1/2}$ for all our results. Here N is the count rate from the surface minus the count rate from the retained, immobile species which was found to be present in all cases. N was normalized to a value of 100 at the start of each experiment, so that slopes would be comparable; t is the time from start of the beam running or from the start of vacuum desorption. This method of plotting has the advantage that the slopes are insensitive to the subtraction made.

When N vs $t^{1/2}$ plots are made for vacuum desorption, Fig. 8, displacement, Fig. 9, and half intensity beams, Fig. 10, a satisfactory and self-consistent situation emerges. Firstly it is shown that temperature enhances rates of vacuum desorption. Acetylene beams enhance the rate of displacement and reaction on the surface with respect to the rates in vacuum, at any given temperature. Most significant of all is the result shown in Fig. 9, which demonstrates that the greatest effect on rate of removal of surface species comes from change in temperature of the surface. The effect of change of temperature on the beam source is very much smaller.

The slopes of the lines are shown in Table 1 together with percentages of retained material.

Half intensity beam effect is shown in Fig. 10. The results are also analyzed in a second way. Figure 11B and C, show the results of subtracting the count from the retained phase and plotting the log (corrected count) against time as a test for first order kinetics. The linearity of the

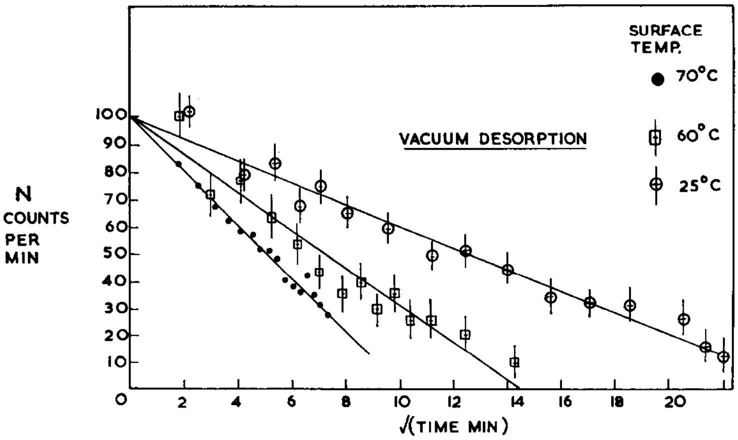


FIG. 8. Desorption into vacuum from palladium films covered by ^{14}C-ethylene: N is counts per minute from surface minus count rate from residual material; the time is measured from start of desorption; standard deviations on counts are shown by vertical heights of symbols.

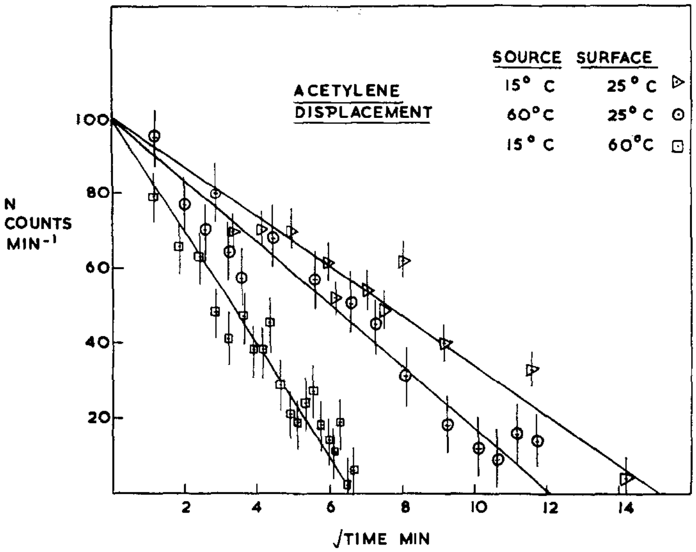


FIG. 9. Displacement of ^{14}C-species from ^{14}C-ethylene-covered palladium by acetylene beam: *N* is counts per minute from surface minus counts per minute from residual material; time measured from start of running beam; standard deviations on counts are shown by vertical heights of symbols.

later stages of both the desorption and acetylene displacement plots is what would be expected for a first order process occurring in each case. In each case these linear stages are preceded by a faster process which is completed relatively quickly. Figure 11A shows a test of first order kinetics in the fast desorption in a case where excellent counting statistics were obtained. Again the plots suggest first order kinetics.

In most cases the counting statistics were such that a clear interpretation in this manner was not possible. $t^{1/2}$ values could not be determined with the confidence required to state activation energies: we may only say that they were in the range 6 to 8 kcal mole^{-1}.

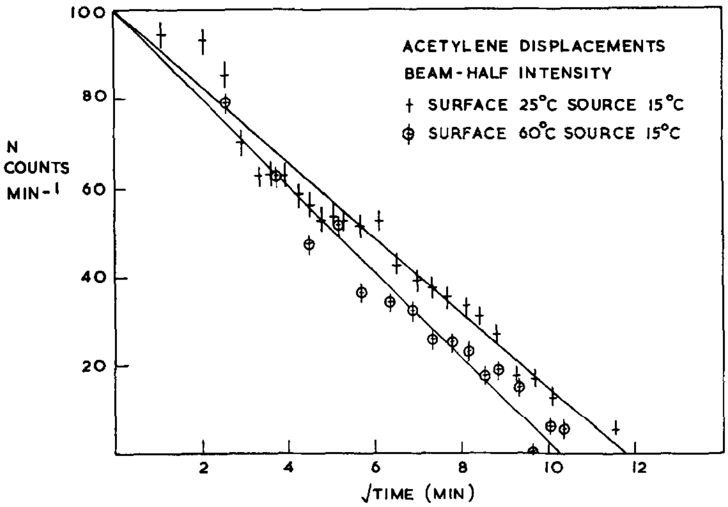


FIG. 10. Displacement of ^{14}C-species from ^{14}C-ethylene-covered palladium by half-intensity acetylene beam: *N* is counts from surface less residual counts; standard deviations on counts are shown by vertical heights of symbols.

TABLE 1

Expt.	Temp		Slope	Retained (%)
	Surface	Source		
Vacuum desorption	25	—	−3.7	70
	15	—	−4.8	—
	60	—	−6.7	71
	70	—	−10.0	—
Acetylene displacement	25	15	−6.7	68
	60	15	−14.3	56
	25	60	−8.3	57
Half-intensity beam: acetylene displacement	25	15	−8.3	61
	60	15	−10.0	37

It was clear that in desorption and displacement that there were three processes occurring: a fast removal of surface species, the α phase, a slower removal, the β phase, and that the surface species could be divided into three kinds: species which left the surface rapidly, species which left more slowly, and firmly retained species: we shall call these the α, β, and γ phases though they are not necessarily the same in each case.

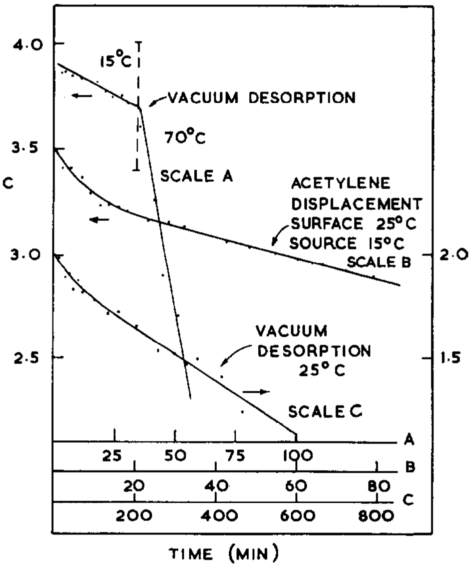


FIG. 11. Plots of log [(surface count rate) − (count rate for retained species)] versus time for desorption into vacuum and acetylene displacement of ^{14}C-species from ^{14}C-ethylene covered palladium.

We consider first the ethylene-covered surface. Stephens (*5*) showed that ethylene reacted with palladium films according to

$$2C_2H_4(g) \rightarrow C_2H_2(ads) + C_2H_6(g).$$

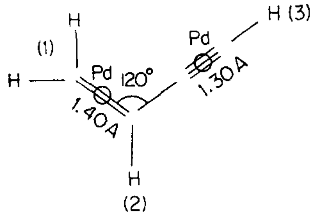
Work in this laboratory (*6*) in a similar system in which ethylene was admitted to a palladium on alumina catalyst at 20°C in a flow system showed the presence of ethane in the eluant.

A mass spectrometric study (*7*) in which ethylene was admitted at low pressure to a palladium film at 23°C revealed that, in addition to self-hydrogenation, small amounts of acetylene and C_3 hydrocarbons could be detected.

Thus the acetylene molecular beam would impinge on a surface covered by acetylene, and acetylenic residues, ethylene, ethane, C_3, and perhaps C_4 hydrocarbons.

Mass spectrometry on the gas withdrawn from the acetylene-beam system confirmed that ethane was present. A fuller investigation in a separate system (*7*) in which acetylene was admitted to a palladium film previously exposed to ethylene showed that the initial displacement products were 65% ethylene; 20% ethane; 10% C_4; and 5% C_3 hydrocarbons. In the later stages of the displacement after 20–30 min the dominant species were 9% C_3, 90% C_4, and 1% C_6 hydrocarbons. The C_4 hydrocarbon was assigned a formula $CH_2{=}CH{-}C{\equiv}CH$ and was probably produced from the units $\underset{\overset{|}{*}}{CH_2{=}CH}$ and $\underset{\overset{|}{*}}{C{\equiv}CH}$. The C_6 hydrocarbon was either $CH{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$ or $H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2$.

Since mass spectrometry also showed two displacement stages, the displacement reactions in the beam system can be postulated to be the same reactions, the α phase being associated principally with acetylene displacement of ethylene, the β phase with the acetylene displacement of C_4 hydrocarbon. Ethylene displacement by acetylene is consistent with the high selectivity exhibited by palladium in hydrogenation of acetylene to ethylene (*8*). The β phase events would seem to represent the coupling of highly unsaturated residue, some from ethylene-^{14}C, some from acetylene: this kind of coupling process has already been suggested (*9*) to account for the hydropolymerization of acetylene. Morrow and Sheppard (*10*) have observed three kinds of CH groups when ethylene is adsorbed on platinum. These were attributed to (1) $M\cdot CH_2$–$CH_2\cdot M$; (2) M_2CH–CH–M_2; and (3) $MCH{=}CHM$. It is worthy of note that the C_4 species in the β phase has three CH groupings which could be distributed on a (100) face of Pd as shown. These may be the CH groups identified by Morrow and Sheppard as (1), (2), and (3).



The retained γ phase probably consists of higher polymers in ring or chain forms.

In both the displacement and desorption experiments we have observed that the surface species resulting from the interaction of ethylene with palladium is heterogeneous in nature: part is reactive, part is retained.

Thus the picture which emerges from the beam experiments is one of acetylene molecules being adsorbed, physically or chemically and taking up the temperature of the surface. Then reaction or displacement takes place during which part of the ^{14}C-labeled species are removed from the surface.

The efficiency of the beam in this process can be calculated approximately as follows: The weight of a typical palladium film was 0.1 to 0.2 mg. This film would take up, according to Stephens (*5*), about 3.7×10^{15} molecules. At 25°C 28% of the surface species was removed in 100 min. During this time 6×10^{16} acetylene molecules from the beam struck the surface, and removed 1.05×10^{15} surface molecules.

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